National Library of Canada

Acquisitions and Bibliographic Services Branch

395 Wellington Street
Ottawa, Ontario
K1A 0N4

Bibliothèque nationale du Canada

Direction des acquisitions et des services bibliographiques

395, rue Wellington
Ottawa (Ontario)
K1A 0N4

Your file Votre référence

Our file Notre référence

NOTICE

The quality of this microform is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us an inferior photocopy.

Reproduction in full or in part of this microform is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30, and subsequent amendments.

AVIS

La qualité de cette microforme dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de qualité inférieure.

La reproduction, même partielle, de cette microforme est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30, et ses amendements subséquents.

Canada

UNIVERSITY OF ALBERTA

POLYPHOSPHATE AND ORTHOPHOSPHATE: INFLUENCE ON THE SORPTION-DESORPTION REACTIONS OF COPPER AND ITS UPTAKE BY WHEAT

By

©

REGI MATHEW

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements for the degree of DOCTOR OF PHILOSOPHY

IN

SOIL CHEMISTRY

DEPARTMENT OF SOIL SCIENCE
EDMONTON, ALBERTA
FALL 1993

National Library
of Canada

Acquisitions and
Bibliographic Services Branch

395 Wellington Street
Ottawa, Ontario
K1A 0N4

Bibliothèque nationale
du Canada

Direction des acquisitions et
des services bibliographiques

395, rue Wellington
Ottawa (Ontario)
K1A 0N4

Your file Votre référence

Our file Notre référence

The author has granted an irrevocable non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of his/her thesis by any means and in any form or format, making this thesis available to interested persons.

The author retains ownership of the copyright in his/her thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without his/her permission.

L'auteur a accordé une licence irrévocable et non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de sa thèse de quelque manière et sous quelque forme que ce soit pour mettre des exemplaires de cette thèse à la disposition des personnes intéressées.

L'auteur conserve la propriété du droit d'auteur qui protège sa thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

ISBN 0-315-88066-X

Canadä

UNIVERSITY OF ALBERTA
RELEASE FORM

NAME OF AUTHOR:	REGI MATHEW
TITLE OF THESIS:	POLYPHOSPHATE AND ORTHOPHOSPHATE: INFLUENCE ON THE SORPTION-DESORPTION REACTIONS OF COPPER AND ITS UPTAKE BY WHEAT
DEGREE:	DOCTOR OF PHILOSOPHY
YEAR THIS DEGREE GRANTED:	1993

Permission is hereby granted to the University of Alberta Library to reproduce single copies of this thesis and to lend or sell such copies for private or scientific research purposes only.

The author reserves all other publication and other rights in association with the copyright in the thesis, and except as hereinbefore provided neither the thesis nor any substantial portion thereof may be printed or otherwise reproduced in any material form whatever without the author's prior written permission

P.O. Box 67051
340 Richmond Road
Ottawa K2A 4E4

October 4, 1993

UNIVERSITY OF ALBERTA
FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled POLYPHOSPHATE AND ORTHOPHOSPHATE: INFLUENCE ON THE SORPTION-DESORPTION REACTIONS OF COPPER IN SOIL AND ITS UPTAKE BY WHEAT submitted by REGI MATHEW in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in SOIL SCIENCE.

M. Nyborg
Marvin Nyborg (Supervisor)

M. J. Dudas
Marvin J. Dudas

J. A. Robertson
James A. Robertson

Gregory Taylor
Gregory J. Taylor

R. César Izaurralde
R. César Izaurralde

R. E. Karamanos
Rigas E. Karamanos (External)

Date: September 9, 1993

Dedicated to my husband Mathew

with love and appreciation

ABSTRACT

Phosphorus is commonly added to soils of western Canada. Research elsewhere has shown that different P sources affect the uptake of Zn in different ways, but little is known about their effects on Cu. Therefore the effect of ammonium polyphosphate (APP) and diammonium phosphate (DAP) on the uptake of Cu by wheat and sorption-desorption reactions of Cu in soil was studied in a Cu deficient soil from Alberta. A greenhouse experiment using wheat (cv. Park) grown in pots showed that application of APP at 40 mg P kg soil^{-1} was better than DAP in increasing the uptake of Cu in the absence of added Cu. When P was added with Cu (10 mg Cu kg soil^{-1}), grain yield was also higher in APP treatments than in DAP treatments. Visual symptoms of Cu deficiency occurred in treatments that received no APP and/or Cu. Three laboratory experiments were conducted to determine the effects of P pretreatment on the sorption-desorption of Cu. In the first, soil samples were equilibrated with APP or DAP at 25, 50 and 75 µmol P g soil^{-1}, then with Cu at 3, 6, 9, 12 and 15 µmol Cu g soil^{-1}. Desorption of P and Cu was done using 0.03M $KClO_4$. Sorption of added APP was greater than added DAP. Pretreatment of soil with DAP as compared to APP resulted in a higher Cu sorption. The amount of sorbed Cu that was subsequently desorbed was greater when the soil was initially treated with APP than with DAP. In the second experiment, sorption of Cu (2, 4, 6, 8 and 10 µg Cu g soil^{-1}) was done for 20, 40, 60 and 80 days after pretreatments with APP or DAP at 15 and 30 µg P g soil^{-1}. The sorption of Cu at different times after the sorption of DAP was also more than that resulted from the sorption of APP. In the third experiment, the rates of P and Cu sorption were studied. Pretreatment of soil with DAP caused a greater rates of Cu sorption than pretreatment with APP. However, the rate of sorption of APP was more than DAP. Another laboratory experiment showed that the activity of Cu-P complexes (calculated using GEOCHEM) in soil solution was not influenced by the sources of P. Both forms of P influenced the surface reactions of Cu on the soil solids more than the Cu-P complex formation in soil solution. In all, application of APP was more beneficial than DAP in increasing the availability of Cu in a Cu deficient soil.

ACKNOWLEDGEMENT

I take the privilege to extend my deep sense of gratitude to my Supervisor, Dr. M. Nyborg, Professor, Department of Soil Science, for his sustained interest, everwilling and constant help during the investigation of this thesis. It is a great pleasure to express my esteemed gratitude to Dr. J. A. Robertson, Chairman, Department of Soil Science, and a member of my Supervisory Committee for his inestimable help, scholarly suggestions and constructive criticisms which aided me in moulding the thesis in a proper way. Their keen interest and support in all my attempts have been much beyond the formal obligation as members of my Supervisory Committee, for which I am greatly thankful to them.

Grateful acknowledgements are also due to Dr. M. J. Dudas, Professor, Department of Soil Science, and Dr. G. J. Taylor, Department of Botany, for their useful suggestions and kind help.

I am especially greatful to Mr. E. D. Solberg for helping me in the collection of soil samples and also for the valuable suggestions.

Appreciation is also expressed to the members of Soil and Animal Nutrition Laboratory, Alberta Agriculture, for giving me necessary help during the chemical analysis of my samples. It is my privilege to thank Mrs. Chung Nguyen and Mr. Michael Abley for their constant help rendered during the Statistical analysis of the data. Special thanks goes to John and Monica for the necessary help provided for the laboratory analysis of samples.

I avail myself of this opportunity to place on record my heartfelt thanks to Mrs. Helen Nyborg for her moral support whenever I needed. Sincere thanks are also to my friends Rupa, Lynette, Yuhuan, Noriko and Xu for their help and encouragement during the preparation of thesis.

It is with an attitude of gratitude and pleasure I remember the strenuous help and unfailing support and constant encouragement of my loving husband Mathew. My special heartfelt thanks to my little Christine for cooperating exceptionally well with me during the preparation of thesis.

I shall fail in my duty if I do not acknowledge the warm blessings and encouragement of our parents, brother Roy, and sisters Alice, Lisie, Elizabeth and Mary which helped me a lot for the successful completion of research work. Special appreciation is extended to our dear uncle Joseph, and aunt Elizabeth for their moral support.

Financial Assistance from Canadian Commonwealth Association, Agriculture Canada and University of Alberta are greatfully acknowledged.

Regi Mathew

TABLE OF CONTENTS

1 INTRODUCTION 1
  1.1 References 6

2 POLYPHOSPHATE AND ORTHOPHOSPHATE: YIELD OF WHEAT AND UPTAKE OF Cu AND P 11
  2.1 Introduction 11
  2.2 Materials and Methods 12
  2.3 Results 14
    2.3.1 Cu Deficiency Symptoms 14
    2.3.2 Yield 15
    2.3.3 Concentration and Uptake of Cu 16
    2.3.4 Concentration and Uptake of P 17
    2.3.5 Concentration and Uptake of Zn 17
    2.3.6 Available P, Cu and Zn in Soil 18
  2.4 Discussion 19
  2.5 Summary and Conclusions 22
  2.6 References 37

3 IMMEDIATE INFLUENCE OF SORBED PHOSPHATES ON THE SORPTION-DESORPTION REACTIONS OF Cu 42
  3.1 Introduction 42
  3.2 Materials and Methods 43
  3.3 Results and Discussion 45
    3.3.1 Sorption of P 45
    3.3.2 Sorption of Cu 45
    3.3.3 Desorption of Cu and P 47
  3.4 Summary and Conclusions 49
  3.5 References 61

4 SORPTION OF Cu AT LOW CONCENTRATION: INFLUENCE OF POLYPHOSPHATE AND ORTHOPHOSPHATE 65
  4.1 Introduction 65
  4.2 Materials and Methods 66
  4.3 Results and Discussion 68
    4.3.1 Sorption of Cu 68
    4.3.2 Desorption of P 71
  4.4 Summary and Conclusions 72
  4.5 References 82

5 KINETICS OF PHOSPHORUS AND COPPER SORPTION: INFLUENCE OF ORTHOPHOSPHATE AND POLYPHOSPHATE 85
  5.1 Introduction 85
  5.2 Theory 86

5.3 Materials and Methods 87
5.4 Results 89
    5.4.1 Kinetics of Cu Sorption 89
    5.4.2 Kinetics of P Sorption 90
5.5 Discussion 91
5.6 Summary and Conclusions 94
5.7 References 105

6 Cu AND P IN SOIL SOLUTION AND THEIR SOLUBILITY CONTROLLING SOLIDS AS AFFECTED BY P SOURCES 107
6.1 Introduction 107
6.2 Materials and Methods 108
6.3 Results 110
    6.3.1 Composition of soil solution 110
    6.3.2 Free ion activity of Cu, $H_2PO_4^-$ and HPO_4^- 110
    6.3.3 Activity of Cu-P complexes 111
    6.3.4 Primary distribution of Cu and P species 111
    6.3.5 Solubility controlling solids 112
6.4 Discussion 112
6.5 Summary and Conclusions 114
6.6 References 130

7 GENERAL DISCUSSION AND CONCLUSIONS 132
6.1 Practical Implications 135
6.2 Future Research 135
6.3 References 136

8 APPENDICES 138

LIST OF TABLES

2.1 Some characteristics of the soil sample (0-15 cm depth) 23

2.2 Influence of incorporated Cu, P and Zn on the yield of total dry matter, straw, grain, and grain to straw ratio at maturity 24

2.3 Influence of incorporated Cu, P and Zn on the mean concentration of Cu, P and Zn in the shoots and, their mean total uptake by wheat in a Cu deficient soil (average of four cuts: 20 days, 40 days, 60 days and maturity) 25

2.4 Orthogonal polynomials showing the response of the concentration and uptake of Cu, P, and Zn by shoots to harvesting times 26

2.5 Influence of incorporated Cu, P and Zn on the concentration of Cu, P and Zn in wheat grain in a Cu deficient soil 27

2.6 Influence of incorporated Cu, P and Zn on the uptake of Cu, P and Zn by grain in a Cu deficient soil 28

2.7 Influence of the incorporated Cu, P and Zn on the concentration of extractable P in soil at different times of harvest 29

2.8 Orthogonal polynomials showing the response of the concentration of extractable P, Cu and Zn in soil to harvest dates 30

2.9 Influence of incorporated Cu, P and Zn on the concentration of DTPA extractable Cu in soil at different times of harvest 31

2.10 Influence of incorporated Cu, P and Zn on the concentration of DTPA extractable Zn in soil at different times of harvest 32

3.1 Influence of the P pretreatments at different concentrations on the mean sorbed P and partition coefficient (Kd) of P 53

3.2 Influence of the P pretreatments on the amount of the subsequently sorbed Cu 54

3.3 Influence of P pretreatment on the Kd of sorbed Cu at different concentrations of added Cu 55

3.4 Influence of the P pretreatments on the desorption of Cu in the third equilibration 56

3.5 Influence of the P pretreatments on the desorption of P in the second and third equilibrations at different amounts of added Cu 57

4.1 The amount of sorbed Cu at different amount of Cu additions at 20, 40, 60 and 80 days after P pretreatment 73

4.2 Contrasts and orthogonal polynomials showing the effect of different amounts of P pretreatments on the sorption of Cu 75

4.3 Influence of time and P pretreatment on the partition coefficient (Kd) of Cu (over all concentrations of Cu) 76

4.4 Desorption of P with different amount of Cu additions at 40, 60 and 80 days after the P pretreatment 77

4.5 Contrasts and orthogonal polynomials showing the response of the mean amount of P desorption to different amounts of application of APP and DAP 79

5.1 Influence of APP and DAP pretreatments on the rate constant (k) for Cu depletion during different time intervals 95

5.2 Influence of APP and DAP pretreatments on the activation energy (Ea), activation enthalpy and negative activation entropy of Cu depletion for 0.25 to 4.00 h reaction period 96

5.3 Influence of P sources on the rate constant (k) for the depletion of P from solution at different time intervals 97

5.4 Influence of P sources on the activation energy (Ea), activation enthalpy, and negative activation entropy for the depletion of P from solution during 0.25 to 8.00 h 98

6.1 Soil solution composition as influenced by P sources and Cu at 20 days . . 115

6.2 Soil solution composition as influenced by P sources and Cu at 40 days . . 116

6.3 Soil solution composition as influenced by P sources and Cu at 60 days . . 117

6.4 Soil solution composition as influenced by P sources and Cu at 80 days . . 118

6.5 Influence of P sources on the free ion activity of Cu, HPO_4^{2-} and $H_2PO_4^-$ (from GEOCHEM) in soil solution at different times of incubation 119

6.6 Influence of P sources on the activity of copper-phosphate complexes in soil solution at different times of incubation 120

6.7 Influence of P sources on the percentage distribution of free and complexed Cu in soil solution at different times of incubation 121

6.8 Influence of P sources on the percentage distribution of phosphate complexes in soil solution at different times of incubation 122

LIST OF FIGURES

2.1 Influence of APP and DAP on the concentration of Cu in wheat shoots at different times of harvest 33

2.2 Influence of P sources and Cu on the total uptake of Cu by wheat at different times of harvest 34

2.3 Influence of P sources and Cu on the concentration of P in wheat shoots at different times of harvest 35

2.4 Influence of P sources and Cu on the total uptake of P by wheat at different times of harvest 36

3.1 to 3.3 Influence of APP and DAP pretreatments at different concentrations on the sorption of the subsequently added Cu 59

3.4 to 3.6 Influence of APP and DAP pretreatments at different concentrations on the desorption of the sorbed Cu 60

4.1 to 4.4 Influence of APP and DAP pretreatments at 15 μg P g soil^{-1} on the sorption of Cu at different times of incubation 80

4.5 to 4.6 Influence of APP and DAP pretreatments at 30 μg P g soil^{-1} on the sorption of Cu at different times of incubation 81

5.1 Rate of Cu depletion at 281 K as influenced by the P pretreatments . 99

5.2 Rate of Cu depletion at 291 K as influenced by the P pretreatments 100

5.3 Rate of Cu depletion at 301 K as influenced by the P pretreatments 101

5.4 Rate of P depletion at 281 K as influenced by the P pretreatments . 102

5.5 Rate of P depletion at 291 K as influenced by the P pretreatments . 103

5.6 Rate of P depletion at 301 K as influenced by the P pretreatments . 104

6.1 Influence of P sources (at 15 μg P g soil^{-1}) and Cu on the pH of the saturated soil solution at different times 123

6.2 Influence of P sources (at 30 μg P g soil^{-1}) and Cu on the pH of the saturated soil solution at different times 124

6.3 Influence of P sources (at 15 μg P g soil^{-1}) and Cu on the ionic strength of the saturated soil solution at different times 125

6.4 Influence of P sources (at 30 μg P g soil^{-1}) and Cu on the ionic strength of the saturated soil solution at different times 126

6.5 Solubility equilibria of some Cu minerals and activity of Cu in saturated soil solution from various treatments 127

6.6 Solubility equilibria of some Fe and Al minerals and activity of Fe and Al in saturated soil solution from various treatments 128

6.7 Solubility equilibria of some phosphate minerals and activity of $H_2PO_4^-$ in saturated soil solution from various treatments 129

LIST OF APPENDICES

1 Chemical analysis of ammonium polyphosphate (APP) 138

2 Procedure used for the microwave digestion (HNO_3-H_2O_2) of wheat samples 139

3 Influence of P sources, Cu and Zn on the total dry matter yield at different times of sampling 140

4 ANOVA for the yield of grain and straw at harvest and grain:straw ratio . 141

5 Influence of P sources, Cu and Zn on the concentration of Cu in shoot at different times of sampling 142

6 Influence of P sources, Cu and Zn on the total uptake of Cu by wheat at different times of sampling 143

7 Influence of P sources, Cu and Zn on the concentration of P in shoots at different times of sampling 144

8 Influence of P sources, Cu and Zn on the total uptake of P by wheat at different times of sampling 145

9 Influence of P sources, Cu and Zn on the concentration of Zn in shoot at different times of sampling 146

10 Influence of P sources, Cu and Zn on the total uptake of Zn by wheat at different times of sampling 147

11 ANOVA for the concentration Cu, P and Zn in wheat grain 148

12 ANOVA for the uptake of Cu, P and Zn by wheat grain 149

13 ANOVA for the concentration of extractable P, Cu and Zn in soil 150

14 ANOVA for the sorbed P and the Kd for sorption of P 151

15 ANOVA for the sorbed Cu and Kd for Cu sorption in the second equilibration, and Cu desorption in third equilibration 152

16 The values of parameters (K and n) in the Freundlich equations for Cu sorption as influenced by the P pretreatments 153

17 ANOVA for the desorbed P in the second and third equilibrations 154

18 ANOVA for the sorption of Cu at 20, 40, 60 and 80 days after the pretreatment with P 155

19 ANOVA for the Kd of sorption of Cu at 20, 40, 60 and 80 days after the pretreatment with P 156

20 The values of parameters (K and n) in the Freundlich equation as influenced by the P pretreatments 157

21 ANOVA for the desorption of P at 40, 60 and 80 days after P pretreatment 158

22 Influence of APP and DAP pretreatment on the mean equilibrium concentration of Cu in solution at different reaction times and temperatures 159

23 Dependence of rate constant (k) on temperature (T) for Cu and P depletion 160

24 Influence of P sources on the mean equilibrium concentration of P at different reaction times and temperatures 161

Chapter 1

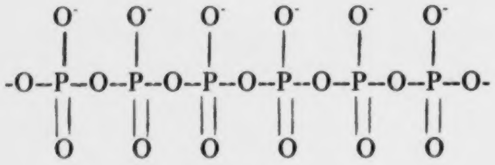
INTRODUCTION

Phosphorus is a commonly-added nutrient to soil because soils are frequently low in plant available P, and the atmosphere essentially supplies none. Orthophosphate is the common form of P used in conventional fertilizers. Orthophosphates, however, may reduce the solubility of micronutrients in soil (Jurinak and Inouye, 1962; Saeed and Fox, 1979; Minzi and Petruzzelli, 1984; Xie and MacKenzie, 1989). On the other hand, some of the linear condensed phosphates (linear polyphosphates) do not precipitate the metals in solution. Although deficiency of Cu is a problem in the Prairie Provinces, research has not been conducted on the reactions of polyphosphates with Cu (Karamanos et al., 1985; Kruger et al., 1985; Karamanos et al., 1986; Penney et al., 1988). Low availability of Cu has been found to reduce grain yield in wheat (Karamanos et al., 1985; Grundon, 1991). Pollen sterility, delayed maturity of grains, and incidence of melanosis and ergot diseases are linked with Cu deficiency (Graham, 1975; Dell, 1981; Piening et al., 1987; Malhi et al., 1987). Since Cu is often added concurrently with P, as a fertilizer to plants, it is important to understand the influence of different forms of P on the partitioning of Cu between soil solids and soil solution.

Ammonium polyphosphates are relatively new phosphatic fertilizers containing P both as condensed linear polyphosphates and orthophosphates. All varieties of condensed phosphates (linear polyphosphates, metaphosphates and ultraphosphates) are formed by repeated condensation of tetrahedral phosphate groups which are linked together through common oxygen atoms and therefore share their corners with similar tetrahedra. The simplest condensed phosphate is the pyrophosphate anion ($P_2O_7^{4-}$) which is formed from the condensation of two orthophosphoric acid molecules.

$$H_3PO_4 + H_3PO_4 \text{ ----> } H_4P_2O_7 + H_2O$$

Linear polyphosphates have a general formula of $P_nO_{3n+1}{}^{(n+2)-}$ and have a chain-like structure:



$$-O-\overset{O^-}{\underset{O}{P}}-O-\overset{O^-}{\underset{O}{P}}-O-\overset{O^-}{\underset{O}{P}}-O-\overset{O^-}{\underset{O}{P}}-O-\overset{O^-}{\underset{O}{P}}-O-\overset{O^-}{\underset{O}{P}}-O-$$

All P-O-P linkages in this structure can be broken (chemically and/or biochemically) and the ultimate products of hydrolysis are discrete orthophosphate ions. Linear polyphosphates are stable in neutral or alkaline solution at room temperature. In general, hydrolytic degradation of long chain polyphosphates proceeds by scission of the end phosphate groups resulting in a rapid accumulation of orthophosphate. In strongly acid solutions, there is also random scission along the chains and thus a given chain may split into two or more.

In polyphosphate chains, a range of P-O-P angles is found giving rotational flexibility about the P-O-P linkage and allowing adjacent tetrahedra to take up alternative orientations. These configurations are determined by the coordination requirements of the cations in solution and the overall packing scheme of the structure. Bond lengths remain fairly constant (Corbridge, 1985). Flexibility of polyphosphate chains in solution is indicated by their ability to form complexes with most metallic cations. This complexing ability is not strongly dependent on chain length and the linear polyphosphates, unlike many anionic complexing agents, are not specific to the coordination requirements of particular cations (Corbridge, 1985).

Polyphosphates have been equal to or superior to the conventional orthophosphate containing fertilizers (Beaton et al., 1962; Adriano and Murphy, 1970; Janssen et al., 1985; Raun et al., 1987). On the other hand, studies of Sutton and Larsen (1964) have shown that condensed phosphates were inferior to orthophosphates as a source of P.

In Alberta, Cu deficiency is more prevalent in organic and sandy soils (Penney et al., 1988). Studies elsewhere have shown that a major part of the soil Cu is complexed with Fe and Al oxides, and organic components (Liang et al., 1991). The high selectivity of organic matter for certain metals suggests that metals coordinate directly with functional groups by forming inner-sphere complexes (Stevenson and Ardakani, 1972). Selectivity coefficients for metal adsorption are dependent on the degree of metal loading and the presence of competing metals (Hendrickson and Corey, 1981). Among the micronutrient cations, Cu forms the most stable organic complexes followed by Zn (Huheey, 1972).

When added to soil, some condensed phosphates increased the concentration of soluble micronutrients and several mechanisms have been suggested (Lindsay et al., 1962; Philen and Lehr, 1967; Hashimoto and Wakefield, 1974; Bar-Yosef and Asher, 1982). Mortvedt and Osborn (1977) attributed the increased concentration of micronutrients in the presence of polyphosphates to the solubilization of soil organic matter. The ability of pyrophosphates to solubilize soil organic matter has been documented (McKeague, 1967; Mnkeni and MacKenzie, 1985; Schnitzer and Schuppli, 1989). Asher and Bar-Yosef (1982) reported that the formation of metal-pyrophosphate complexes occurred only under high rates of application. However, information on the influence of polyphosphates on the uptake of P and Cu by crops grown in a Cu deficient soil is lacking.

Phosphates also influence the sorption-desorption reactions of trace elements on soil solids and speciation in the soil solution (Bolland et al., 1977; Clark and McBride, 1985; McBride, 1985; Shuman, 1986). The process of sorption includes adsorption and surface precipitation reactions resulting from heterogeneous nucleation (Sposito, 1985). The adsorbing components in the soil can catalyze heterogeneous nucleation reactions by lowering the activation energy required for nucleation (Corey, 1981). The catalytic effect of a solid surface is due to the interfacial energy between the two solids being lower than the interfacial energy between the crystal and the solution (Stumm and Morgan, 1970). However, all solid surfaces will not catalyze the same reaction to the same extent. Sorption depends on lattice matching, which is a function of the orientation of molecules on the surface. Since polyphosphate and orthophosphates have different structures there is a possibility that these two forms of P will affect the sorption reactions of metals in different ways.

Sorption of P onto the soil mineral surfaces results in a change in their surface characteristics (Saeed and Fox, 1979; Gillman and Fox, 1980; Pardo and Guadalix, 1990). When P is introduced into the soil, there are at least four processes that perturb the equilibria of the micronutrient metals: " 1) a shift in the pH due to the fertilizer dissolving in soil solution; 2) a shift in pH due to the reactions of both the phosphate and the associated cations with soil components; 3) changes in the surface charge due to the adsorption of the phosphates on to the colloids; 4) precipitation of micronutrient metals with phosphates" (Shuman, 1988). Since the sorbed phosphates change the surface characteristics of soils (especially those containing amorphous oxides), they will also affect the sorption-desorption reactions of the subsequently added cations (Bolland et al., 1977; McBride, 1985).

Sorption reaction rates of ions in soil are initially fast (minutes or hours), but diminish (days or weeks) with time (Riemsdijk and Haan, 1981; Bolan et al., 1985; Sparks, 1985). This can be caused by changes in the structure of adsorbate/adsorbent with time or by processes like diffusion. Unlike orthophosphates, the structure of polyphosphates could alter with time because of hydrolysis, and their reactions in solution depend on the chain length. Consequently it is necessary to investigate the changes in the sorption of Cu on the different phosphated surfaces at different times.

Along with the time of reaction, concentrations of added solutes also influence the mechanisms of sorption, because the adsorbing components in the soil are heterogeneous and have binding sites with different bonding energy (McBride, 1982; McBride et al., 1984; Clark and McBride, 1984). Therefore the sorption reaction mechanisms of P and Cu depend on their concentrations.

The subsequent availability of solutes added at low concentrations depends on the extent of desorption from the solid phase. The reactions of P and Cu with soil are slowly reversible processes and the equilibrium favours sorption (McLaren and Crawford, 1974 ; McBride et al., 1984; Pardo and Guadalix, 1990). The energy needed for desorption is high and is dependent on the energy of adsorption and the activation energy

(Adamson, 1976). The hysteresis observed in sorption-desorption processes indicates that the desorption is slower and that insufficient time has been allowed for the process to complete, and/or the occurrence of further processes following adsorption (Barrow, 1985; McBride, 1989). The extent of desorption of the sorbed trace elements from the phosphated and non-phosphated surfaces could vary depending on the energy of adsorption.

In many instances, sorption processes are described by adsorption isotherm equations. These equations were originally developed for pure systems and/or for the adsorption of gases. The use of constants in the adsorption isotherm equations (e.g. Langmuir's), for describing the physical and chemical characteristics of the adsorbents and the adsorbate in soil systems is questioned by many soil scientists (Veith and Sposito, 1977; Sibbesen, 1981; Travis and Etnier, 1981). Assumptions of these equations are not valid for soil systems and some of them are empirical in nature. These are the reasons for their unsuitability to describe the sorption mechanisms in soil. The fitting of experimental sorption data to an adsorption isotherm equation provides no evidence for the actual mechanism of a sorption process (Sposito, 1984). In such situations, kinetic equations are more appropriate to calculate the activation energy (Moore, 1982) and to describe the intensity of sorption reactions.

Conventional chemical soil test results cannot explain the processes controlling the solubility of nutrients in soil. In many cases soil test values will not give good correlation with the crop response, partly because of the rhizosphere influence. Hence, growth chamber and field studies along with laboratory incubation experiments are necessary to assess the metal availability in soil. However, little work has been reported on the influence of added orthophosphate and polyphosphate on the solubility of Cu in soil, particularly in terms of surface reactions and reactions in soil solution. Studies on the interactions of P and Cu on the soil solids and in soil solution will provide a better insight into the reactions of P and Cu fertilizers in soil. Recognizing the importance of surface chemistry and soil solution chemistry for describing the P-Cu interactions in a Cu deficient soil, laboratory incubation and greenhouse experiments were conducted with the following objectives of finding:

1) the effect of ammonium polyphosphate (APP) and diammonium phosphate (DAP) on the yield of wheat and uptake of Cu and P in a Cu deficient soil,
2) the immediate influence of the sorption of APP and DAP at different amounts on the sorption-desorption reactions of Cu,
3) the changes in the sorption of Cu at different times after the addition of APP and DAP at low concentration, and
4) the influence of sorption of APP and DAP on the kinetics of Cu sorption.
5) the changes in the soil solution Cu-P complexes at different times following the application of APP and DAP

1.1 REFERENCES

Adamson, A.W. 1976. Physical chemistry of surfaces. 3rd ed., Wiley-Interscience, New York.

Adriano, D.C., and L.S. Murphy .1970. Effect of ammonium polyphosphate on yield and chemical composition of irrigated corn. Agron. J. 62: 561-567.

Asher, L.E., and B.Bar-Yosef. 1982. Effect of pyrophosphate, EDTA and DTPA on Zn sorption by montmorillonite. Soil Sci. Soc. Am. J. 46: 271-274.

Bar-Yosef, B., and L.E. Asher. 1982. Reactions of pyrophosphate in soils and its effect on Zn sorption at various pH levels. Soil Sci. 136: 82-88.

Barrow, N.J. 1985. Reactions of anions and cations with variable-charge soils. Adv. Agron. 38: 183- 230.

Beaton, J.D., D.W.L. Read, and W.C. Hinman. 1962. Phosphorus uptake by alfalfa as influenced by phosphate source and moisture. Can. J. Soil Sci. 42: 254-258.

Bolan, N.S., N.J. Barrow, and A.M. Posner. 1985. Describing the effect of time on the sorption of P by iron and aluminium hydroxides. J. Soil Sci. 36: 187-197.

Bolland, M.D.A., A.M. Posner, and J.P. Quirk . 1977. Zinc adsorption by goethite in the absence and presence of phosphate. Aust. J. Soil Res. 15: 279-286.

Clark, C.J., and M.B. McBride. 1984. Chemisorption of Cu(II) and Co(II) on allophane and imogolite. Clays Clay Miner. 32: 300-310.

Clark, C.J., and M.B. McBride. 1985. Adsorption of Cu(II) by allophane as affected by phosphate. Soil Sci. 139: 412-421.

Corbridge, D.E.C. 1985. Phosphorus: An outline of its chemistry, biochemistry and technology. 3rd ed. Elsevier Sci. Publishers, New York.

Corey, R. B. 1981. Adsorption vs precipitation. p. 161-182. *In* M. A. Anderson and A. J. Rubin (ed.) Adsorption of inorganics at solid-liquid interfaces. Ann. Arbor. Science Publishers Inc. U.S.A.

Dell, B. 1981. Male sterility and wall structure in copper deficient plants. Ann. Bot. 48: 599-608.

Gillman, G.P., and R.L. Fox. 1980. Increases in the cation exchange capacity of variable charge soils following superphosphate applications. Soil Sci. Soc. Am. J. 44: 934-938.

Graham, R.D. 1975. Male sterility in wheat plants deficient in copper. Nature. 254: 514-515.

Grundon, N.J. 1991. Copper deficiency of wheat: Effect of soil water content and fertilizer placement on plant growth. J. Plant Nutr. 14: 499-509

Hashimoto, I., and Z.T. Wakefield. 1974. Hydrolysis of pyrophosphate in soils. Response to temperature and effect on heavy metal uptake by plants. Soil Sci. 118: 90-94.

Hendrickson, L.I., and R.B. Corey. 1981. Effect of equilibrium metal concentrations on apparent selectivity coefficients of soil complexes. Soil Sci. 131: 163-171.

Huheey, J.E. 1972. Inorganic chemistry: Principles of structure and reactivity. Harper and Row, NewYork.

Janssen, K .A., D.A. Whitney, and D.E. Kissel. 1985. Phosphorus application frequency and sources for grain sorghum. Soil Sci. Soc. Am. J. 49: 754-757.

Jurinak, J.J., and T.S. Inouye. 1962. Some aspects of Zn and Cu phosphate formation in aqueous systems. Soil Sci. Soc. Am. Proc. 26: 144-147.

Karamanos, R.E., J. G. Fradette, and P.D. Gerwing. 1985. Evaluation of Cu and Mn nutrition of spring wheat grown on organic soils. Can. J. Soil Sci. 65: 133-148.

Karamanos, R.E., G. A. Kruger, and J. W. B. Stewart. 1986. Copper deficiency in cereal and oilseed crops in northern prairie soils. Agron. J. 78: 317-323.

Kruger, G.A ., R. E. Karamanos, and J. P. Singh. 1985. The Cu fertility of Saskatchewan soils. Can. J. Soil Sci. 65: 89-99.

Liang, J., W. B. Stewart, and R. E. Karamanos. 1991. Distribution of soil Cu fractions in Saskatchewan. Can. J. Soil Sci. 71: 89-99.

Lindsay, W.L., A.W. Frazier, and H.F. Stephenson. 1962. Identification of reaction products from P fertilizers in soils. Proc. Soil Sci. Soc. Am. 26: 446-452.

Malhi, S.S., L.J. Piening, and D.J. MacPherson. 1987. Effect of Cu on stem melanosis of Park wheat. p. 17-18. *In* Proc. of 24th Annual Alberta Soil Sci. Workshop. Calgary, Alberta. Feb 17-18 , 1987.

McBride, M. B., A.R. Fraser, and W.J. McHardy. 1984. Cu^{2+} interaction with microcrystalline gibbsite. Evidence for oriented chemisorbed Cu ions. Clays Clay Miner. 32: 12-18.

McBride, M. B.1982. Cu^{2+} adsorption characteristics of aluminum hydroxide and oxyhydroxides. Clays Clay Miner. 30: 21-28.

McBride, M.B. 1985. Sorption of Cu(II) on aluminum hydroxide as affected by phosphate. Soil Sci. Soc. Am. J. 49: 843-846

McBride, M.B. 1989. Reactions controlling heavy metal solubility in soils. p. 1-47. *In* Stewart, B.A.(ed.) Adv. in Soil Science. Vol.10. Springer Verlag, New York

McKeague, J.A. 1967. An evaluation of 0.1M pyrophosphate and pyrophosphate-dithionite in comparison with oxalate as extractants of the accumulation products in podzols and some other soils. Can. J. Soil Sci. 47: 96-99

McLaren, R.G., and D.V. Crawford. 1974. Studies on soil Cu III. Isotopically exchangeable Cu in soils. J.Soil Sci. 25: 111-119.

Minzi, L.R., and G. Petruzzelli. 1984. The influence of P fertilizers on Cd solubility in soil. Water Air and Soil Pollution. 23: 423-429.

Mnkeni, P.N.S., and A.F. MacKenzie. 1985. Retention of ortho- and polyphosphates in some Quebec soils as affected by added organic residues and calcium carbonate. Can. J. Soil Sci. 65: 575-585.

Moore, W.J. 1982. Basic physical chemistry. Prentice- Hall Inc. New Jersey.

Mortvedt, J. J. and G. Osborn. 1977. Micronutrient concentration in soil solution after ammonium phosphate applications. Soil Sci. Soc. Am. J. 41: 1004-1009.

Pardo, M.T., and M.E. Guadalix.1990. Phosphate sorption in allophanic soils and release of sulphate, silicate and hydroxyl . J. Soil Sci. 4: 607-612.

Penney, D.C., E.D. Solberg, and I.R. Evans. 1988. The Cu fertility of Alberta soils. p. 125-133. *In* Proc. of 25th Annual Alberta Soil Sci. Workshop. Lethbridge, Alberta. Feb. 23- 24.

Philen, O.D., and J.R. Lehr. 1967. Reactions of ammonium polyphosphate with soil minerals . Proc. Soil Sci. Soc. Am. 31: 196-199.

Piening, L.J., D.J. MacPherson, and S. S. Malhi. 1987. The effects of Cu in reducing stem melanosis of Park wheat. Can J. Plant Sci. 67: 1089-1091.

Raun, W.R., D.H. Sander, and R.A. Olson. 1987. Phosphorus fertilizer carriers and their placement for minimum till corn under sprinkler irrigation. Soil Sci. Soc. Am. J. 51: 1055-1062.

Riemsdijk, V.W.H., and D.F.A.M. Haan. 1981. Reaction of orthophosphate with a sandy soil at constant supersaturation. Soil Sci. Soc. Am. J. 45: 261-266.

Saeed, M., and R.L. Fox. 1979. Influence of phosphate fertilization on Zn adsorption by tropical soils. Soil Sci. Soc. Am. J. 43: 683-686.

Schnitzer, M. and P. Schuppli. 1989. The extraction of organic matter from selected soils and particle size fractions with 0.5 M NaOH and 0.1 M $Na_4P_2O_7$ solutions. Can. J. Soil Sci. 69: 253-262.

Shuman, L.M. 1986. Effect of ionic strength and anions on Zn adsorption by two soils. Soil Sci. Soc. Am. J. 50: 1438-1442.

Shuman, L. M. 1988. Effect of phosphorus level on extractable micronutrients and their distribution among soil fractions. Soil Sci. Soc. Am. J. 52: 136-141.

Sibbesen, E. 1981. Some new equations to describe phosphate sorption by soils. J. Soil Sci. 32: 67-74.

Sparks, D.L. 1985. Kinetics of ionic reactions in clay minerals and soils. Adv. Agron. 38: 231-266.

Sposito, G. 1984. The surface chemistry of soils. Oxford University Press. New York. 122-124.

Sposito, G. 1985. Distinguishing adsorption from surface precipitation. p. 217-228. *In* J. A. Davis, and K. F. Hayes (ed.) Geochemical processes at mineral surfaces. Am. Chem. Soc. Symposium Series. No. 323. Am. Chem. Soc. Washington.

Stevenson, F.J., and M.S. Ardakani. 1972. Organic matter reactions involving micronutrients in soils. p.79-114. *In* J.J. Mortvedt, P.M. Giordano, and W.L.Lindsay (ed.) Micronutrients in agriculture. Proc. Symposium Soil Sci. Soc. Am. and T.V.A. Muscle Shoals, U.S.A. April 20- 22, 1971.

Stumm, W., and J.J. Morgan. 1970. Aquatic chemistry. Wiley- Interscience, NewYork. 11-12

Sutton, C.D., and S. Larsen. 1964. Pyrophosphate as a source of P for plants. Soil Sci. 97: 196-201

Travis, C.C., and E.L. Etnier. 1981. A survey of sorption relationships for reactive solutes in soil. J. Environ. Qual. 10: 8-17.

Veith, J.A., and G. Sposito. 1977. On the use of the Langmuir equation in the interpretation of "adsorption" phenomena. Soil Sci. Soc. Am. J. 41: 697-702.

Xie, R.J., and A.F. MacKenzie. 1989. Effects of sorbed orthophosphate on Zn status in three soils of eastern. Can. J. Soil Sci. 40: 49-58.

Chapter 2

POLYPHOSPHATE AND ORTHOPHOSPHATE: YIELD OF WHEAT AND UPTAKE OF Cu AND P

2.1 INTRODUCTION

Copper deficiency, often found in organic and sandy soils, is an important micronutrient problem with cereal grain production in Alberta (Penney et al., 1988). There are several reasons for the occurrence of the Cu deficiency. First, low total Cu content of the soil. Secondly, formation of stable complexes of Cu with soil organic matter (McLaren and Crawford, 1973). Thirdly, interaction of Cu with orthophosphates (Bingham et al., 1958; Bingham and Garber 1960), which are the common form of P in conventional fertilizers. Therefore it will be advantageous to find an alternative P source which could increase the availability of Cu to plants.

Polyphosphates are relatively new phosphatic fertilizers containing a mixture of linear polyphosphate and orthophosphate forms. They have been reported to be a suitable source of P for plants (Dick and Tabatabai, 1987; Raun et al., 1987). Further, the structure of some of the condensed phosphates allow them to form soluble metal complexes in solution (Corbridge, 1985). The ability of condensed phosphates to coordinate with metals influences the reactions of metals in soil and their availability to plants (Hashimoto et al., 1969; Khasawneh et al., 1974). For example, the mobility and effectiveness of added Zn was greater when applied with polyphosphate rather than orthophosphate (Mortvedt and Giordano, 1967, 1969 and 1975). Asher and Bar-Yosef (1982) suggested that the increased solution concentration of Zn found in the pyrophosphate-treated soils was due to organic matter solubilization and Zn complex formation with pyrophosphate.

A greater uptake of metals by corn was found by Hashimoto and Wakefield (1974) when the crop was fertilized with pyrophosphate than with orthophosphate. Showk et al., (1987) reported a decrease in the DTPA extractable Fe, Cu, and Mn with the addition of monoammonium phosphate and monocalcium phosphate, while high levels of ammonium polyphosphate (APP) increased the available Fe, Cu and Mn in soil. In addition to the direct formation of metal complexes in solution, polyphosphates solubilize soil organic matter (Mnkeni and MacKenzie, 1985; Schnitzer and Schuppli, 1989). This solubilization may help in the release of some strongly bound metals, like Cu, and increase their bioavailability (Huheey, 1972).

Another approach to increase the availability of Cu is to displace the exchangeable Cu and fill the sorbing sites with metals having high affinity. Among the micronutrient cations, Zn has the second highest affinity (following Cu), for metal oxides, silanol groups and organic components (Kinniburgh et al., 1976, Schindler et al., 1976; Huheey, 1972). So, some of the exchangeable Cu might be displaced by the addition of Zn. Kurdi and Doner (1983) found that when the concentration of added Zn was 10 times the concentration of added Cu, the amount of sorbed Cu tended to decrease. Consequently, Zn was included in my study based on the assumption that added Zn would replace some of the exchangeable Cu, and occupy high affinity adsorbing sites so that the solubilized Cu would not be immobilized. Therefore the objective of this experiment was to find the influence of APP and diammonium phosphate (DAP) on yield and uptake of Cu and P in the absence and presence of added Cu and Zn on a Cu deficient soil.

2.2 MATERIALS AND METHODS

A surface soil sample (0 - 15 cm) was collected from a Cu responsive Eluviated Black Chernozemic soil, developed on a coarse textured alluvial-lacustrine material, situated approximately 50 km south east of Edmonton (legal location SW 20- 47- 24-W4). Air dried and sieved (2mm) soil (1.25 kg) was placed in pots (11 cm diameter 15 cm high) without drainage holes. Nine nutrient treatments were applied in three replications: control, APP alone, DAP alone, Cu alone, Zn alone, APP+Cu, APP+Zn, DAP+Cu, and DAP+Zn. Thus, there were 27 experimental units at each time of harvest. Phosphorus was added at 40 mg P kg soil^{-1} as APP or DAP. Zinc and Cu were added at 10 mg Zn or Cu kg soil^{-1} as $ZnSO_4.7H_2O$ or $CuSO_4.5H_2O$. Solution APP was obtained from Tennessee Valley Authority, Muscle Shoals, Alabama. Sources of DAP, Cu and Zn were analytical grade salts. The analysis of the APP solution is given in Appendix 1. A blanket application of nitrogen (100 mg N kg soil^{-1} as NH_4NO_3), potassium (50 mg K kg soil^{-1} as KCl) and sulphur (20 mg S kg soil^{-1} as Na_2SO_4) was made to all treatments. The nutrients were dissolved in water and incorporated uniformly with the soil. The experiment was laid out in a randomized design using wheat (cv. Park) as the test crop. Within a day of fertilization, 10 seeds were sown in each pot, and one week after emergence thinned to 5 plants per pot. Greenhouse temperatures ranged between 20 to 25° C and artificial lighting was provided for 14 hours daily. Distilled water was added each day sufficient to bring the soil moisture up to 70 per cent of the moisture held at field capacity.

Plants were harvested at 20 day intervals until maturity (20, 40, 60 days and at maturity), by cutting at soil surface. Straw and grain were harvested separately at maturity. Plant samples were dried at 65° C, weighed for dry matter determination, ground and subjected to microwave digestion (HNO_3- H_2O_2) (adapted from White and Douthit, 1985) for the determination of P, Cu and Zn. Details of the procedure are given in Appendix 2. Concentrations of P, Cu and Zn in straw and grain were measured separately at maturity. Total uptake of nutrients at maturity included the uptake by straw and grain.

At each harvest, soil samples were taken before drying, for the determination of available P, Zn, and Cu, but the results were expressed on an oven dry basis. Available Cu and Zn were extracted with DTPA extractant at pH 7.3 (Lindsay and Norvell, 1978) and the total contents in extract were measured by Inductively Coupled Plasma Atomic Emission Spectroscopy. Available P was determined using the Miller and Axley method (1956).

Textural analysis of the bulk soil sample was done using the pipette method (Gee and Bauder, 1986) and organic C was estimated by dry combustion in a Leco furnace (Nelson and Sommers, 1982). Total cation exchange capacity was determined by the NH_4OAc method (McKeague 1978) and perchloric-nitric acid digestion was used for the total P, Cu, Zn and Fe content in soil. Different fractions of Fe and Al [Pyrophosphate extractable Fe (Pyro-Fe), Pyrophosphate extractable Al (Pyro-Al), Ammonium oxalate extractable Fe (Ox-Fe), Ammonium oxalate extractable Al (Ox-Al), and Citrate-Bicarbonate-Dithionite extractable Fe (CBD-Fe), Citrate-Bicarbonate-Dithionite extractable Al (CBD-Al)] were determined by the methods described by McKeague, 1978. Some physical and chemical properties of the bulk soil sample are given in Table 2.1.

Statistical analysis of data

Analysis of variance at each time of harvest (27 experimental units with nine treatments and three replications) and also over four time intervals (108 experimental units) for yield, nutrient uptake and concentration in plants and available nutrients in soils was performed using PROC GLM in SAS (SAS Institute, 1987). Homogeneity of error variance was tested by plotting the residuals against the predicted values using PROC PLOT, and the normality of error was tested using PROC UNIVARIATE. Comparisons of treatment means at each harvest date were made using LSD. Treatment x Time interaction means were compared by the lsmeans/pdiff option in PROC GLM. Orthogonal polynomials for the treatments were calculated to determine the response of nutrient concentration and nutrient uptake to time of harvest. Contrasts were used for comparing various treatment groups with respect to the dry matter yield, nutrient uptake, and nutrient concentration.

2.3 RESULTS

2.3.1 Cu DEFICIENCY SYMPTOMS

Visual symptoms of Cu deficiency occurred on young leaves and at flowering. Rolling of young leaf tips followed by wilting and necrosis was observed just a month after seeding, but slowly disappeared. Flowering was delayed and grains were often not filled or were partially filled in the affected plants. These symptoms were severe in treatments which had not received Cu and/or APP.

2.3.2 YIELD

Although the above ground biomass was measured at four harvesting days (Appendix 3 and 4), only the total yield (straw + grain) at maturity was discussed here. Total dry matter yield at maturity was affected significantly by various treatments (Appendix 4). Addition of APP (with or without added Cu) increased total yield over the control, while DAP increased the total yield only when added with Cu (Table 2.2). The highest total yield occurred when Cu was added with APP and DAP. Zinc increased the total yield over the control when added with APP and DAP as compared to the addition of Zn alone.

Grain yield was increased relative to the control by the application of APP alone as against the DAP alone treatment (Table 2.2). Copper added alone or with either P source resulted in an increase of grain yield. The difference between forms of P in the presence of Cu was small compared to the P alone treatments. Application of Zn increased the grain yield over the control except when added with DAP.

Straw yield at maturity was not affected by various treatments, but grain:straw ratio differed among treatments (Table 2.2). Copper addition alone, or with P, increased the grain:straw ratio as compared to the control, P alone, and Zn alone treatments.

Contrasts showed that addition of APP as compared to DAP resulted in a higher yield of total dry matter and grain at maturity (Table 2.2).

2.3.3 CONCENTRATION AND UPTAKE OF Cu

Concentration of Cu in shoot (above ground vegetative part) was affected by fertilizer treatment and harvesting days. Highest mean concentrations of Cu (average of 4 cuts at 20, 40, 60 days and at maturity) in shoot were in the APP+Cu and Cu alone treatments, followed by DAP+Cu treatment (Table 2.3). The mean Cu concentration of APP+Cu treatment was 29 per cent greater than DAP+Cu treatment, and without added Cu the concentration from APP treatment was 42 per cent more than DAP treatment.

Treatment x Time interaction was significant for the concentration of Cu in shoot (Appendix 5). There were different trends in the Cu concentration of the shoot with time.

At 20 days, the highest Cu concentration (10 mg Cu kg^{-1}) occurred in the Cu alone treatment, but there was a marked decrease by day 40, and a gradual decline thereafter, giving a quadratic response to harvesting time (Table 2.4, orthogonal polynomials; Fig. 2.1). Copper concentration in DAP alone and DAP+Cu treatments also showed a decrease with time, but the response to harvesting time was linear. By contrast, in the control treatment, there was an increase in the concentration of Cu at second harvest and then a subsequent decrease. The concentrations in APP treatments (APP alone and APP+ Cu) were generally above the other treatments from the second harvest and onwards (Fig. 2.1 and Appendix 5). Concentration of Cu in the control, APP alone, and APP+Cu treatments had a cubic response to harvesting time. The DAP alone treatment resulted in Cu concentrations essentially the same as the control except for the second harvest. In a general way the Cu treatments resulted in greater Cu concentration than the non-Cu treatments.

Maximum mean total uptake of Cu (average of 4 cuts at 20, 40, 60 days and at maturity) occurred in the APP+Cu treatment (5.70 µg Cu $plant^{-1}$), but values for Cu alone and DAP+Cu were only slightly lower (Table 2.3). Without Cu addition, mean total uptake was greater with APP compared to DAP. Addition of Zn alone resulted in a higher mean total uptake of Cu than when P and Zn were added together. Contrasts showed that APP resulted in greater total uptake of Cu than did DAP. In all the treatments, except Cu alone and APP+Cu, total uptake increased gradually up to 60 days after sowing and then decreased (Fig. 2.2, Appendix 6). However, the orthogonal polynomials showed a cubic response of total uptake to harvesting times for all the treatments except the APP alone, APP+Cu and APP+Zn (Table 2.4) Total uptake in all the APP treatments showed a quadratic response.

Application of Cu alone (4.69 mg Cu kg^{-1}) resulted in the highest concentration of Cu in the grain, followed by APP+Cu treatment and DAP+Cu (Table 2.5). Ammonium polyphosphate when added with Zn had higher Cu concentration than DAP+Zn treatments. Greater concentration was in Zn alone treatment as compared to DAP alone treatment, but not significantly different than the control. In general, APP treatments had higher concentration of Cu in grain than DAP treatments (contrasts).

Highest uptake of Cu by grain occurred when Cu was added alone and with APP, and then followed by DAP+Cu treatment (Table 2.6). However, in the absence of added Cu and Zn, APP increased the uptake of Cu by grain while DAP tended to decrease it. In the presence of Zn, APP and DAP had similar uptake values. Treatments with Zn alone had higher uptake than the control and when Zn was added with DAP.

2.3.4 CONCENTRATION AND UPTAKE OF P

Sources of P and the age of the plant influenced the concentration and uptake of P by shoots (Appendix 7 and 8). Addition of either form of P increased the concentration and uptake as compared to the control treatment. At all sampling times, the concentrations of P in shoots, and grain at maturity were higher in DAP treatments than in APP treatments (Fig. 2.3, Table 2.3, 2.5, and Appendix 7). Similar to concentration, uptake of P by shoots and grain were higher in DAP treatments than in APP treatments (Fig. 2.4, Table 2.6, and Appendix 8). Treatments where Cu was added with APP or DAP tended to have less P concentration in grain than where Zn was added with APP or DAP. However the P uptake by grain was higher in the P+Cu treatments than in P+Zn treatments (Table 2.6, contrasts). The concentrations of P in shoots at different harvest times, and in grain in the Zn alone or Cu alone treatments were similar to the control values (Fig. 2.3, and Appendix 7).

There was a linear or quadratic decrease with time in the concentration of P in shoot in all treatments (Table 2.4). In all the treatments the response of total uptake to harvesting time was linear or quadratic (Table 2.4)

2.3.5 CONCENTRATION AND UPTAKE OF Zn

Application of Zn increased the mean concentration of Zn in shoots (Table 2.3). The mean Zn concentrations in shoots were not affected by the form of P (contrasts). By contrast, treatments where Zn was added with P resulted in a greater Zn uptake than when Zn was added alone.

Uptake of Zn by grain was higher than the control when Zn was added with APP and DAP, but not when Zn was added alone (Table 2.6). When Cu was added, both the concentration and uptake of Zn in the shoots and grain tended to be less than when P was added alone (Table 2.3, 2.5, 2.6; Appendices 9 and 10), even though the dry matter increased in the presence of Cu .

2.3.6 AVAILABLE P, Cu AND Zn IN SOIL

Extractable (available) P content in soil was higher at all harvest dates in treatments which received DAP as compared to APP, and they were both greater than the control (Table 2.7). Only at 20 days, was P concentration in Zn or Cu treatments higher than the control. There was no difference in the extractable P content when P was added with Cu and when added with Zn (contrasts). Treatment x Time interaction was significant for the extractable P content (Appendix 13). In all the treatments (except the Cu alone and Zn alone), the extractable P showed a quadratic or cubic decrease with time of harvesting (Table 2.8).

The DTPA extractable (available) Cu was higher at all harvest dates, in treatments with added Cu than in the control (Table 2.9). There was no difference between P+Cu and Cu alone treatments with respect to the available Cu content (contrasts). Concentration of Cu was higher in APP treatments than DAP treatments. Addition of Zn alone decreased the Cu concentration below that of the control at 20 and 60 days. Orthogonal polynomials for the response of the extractable Cu content to harvesting days showed a quadratic or cubic response in all the treatments, except for the APP alone treatment (Table 2.8 and 2.9).

Available (DTPA extractable) Zn was greater when Zn was added alone or with P as compared to the other treatments (Table 2.10), and there was no difference between P+Zn and the Zn alone treatments (contrasts). At 20 days, all the treatments had higher available Zn than the control treatment, while at later dates, higher values were shown only by the treatments which received Zn. APP+ Zn had greater mean available Zn than DAP+Zn.

2.4 DISCUSSION

The total content of Cu in the test soil sample falls within a range reported for the surface samples of some Alberta soils (Soon and Abboud, 1990), and was lower than that reported for the surface horizons of Chernozems (Dudas and Pawluk, 1980). The DTPA extractable Cu in the experimental soil was below the critical level for Cu deficiency in the Prairie Provinces (Kruger et al., 1985; Karamanos et al., 1986; Penney et al., 1988). Other nutrients were marginal to high (Soil and Animal Nutrition Laboratory, Alberta Agriculture). Thus, the major limiting factor for wheat growth in the experimental soil was the insufficient amount of bioavailable Cu.

In my study, the grain yield was reduced by Cu deficiency, but not the straw yield. This was in agreement with the findings of Nambiar (1976). He found increasing grain yield as the Cu supply was increased, even though the straw yield was only slightly enhanced. The reason for the decreased grain yield under Cu deficiency may be related to the mobility of Cu within the plant and its role in pollen synthesis. Copper is not readily remobilized within the plant, when a deficiency occurs because of complex formation with amino compounds (White et al., 1981). Consequently, with Cu deficiency the movement of Cu to flowers, where it is required for optimal seed set, is delayed or restricted. In addition, under Cu deficiency, only a limited number of viable pollen grains is produced and poor lignification of anther cell walls delays or inhibits the release of pollen grains (Graham, 1975; Dell, 1981). These effects might have resulted in a poor fertilization and seed set, with unfilled grain and partially filled heads, in my Cu deficient treatments. However, the symptoms of melanosis commonly associated with Cu deficiency in Park wheat (Malhi et al., 1987; Piening et al., 1989) were not observed in the Cu deficient plants.

Without added Cu, high yields and satisfactory growth were obtained when APP was added. This result may be explained by the solubilization of soil organic matter and release of soil Cu by APP for plant uptake (Mnkeni and MacKenzie, 1985; Schnitzer and Schuppli, 1989). In addition, incubation experiments (Chapter 3 to 5) showed a lower sorption of added Cu following pretreatment with APP than with DAP, leading to higher soluble Cu in soil solution and hence higher Cu uptake. Studies of Giordano and Mortvedt (1969); Mortvedt and Giordano (1969, 1975) and Hashimoto and Wakefield (1974) also found a greater uptake of micronutrients with polyphosphate application.

High concentration of Cu in shoots occurred only when Cu or APP was added. As a result, the extent of remobilization of Cu to the grain may have been greater in these treatments because the remobilization of micronutrients in the flowering stage depends on their concentration in the leaves (Loneragan et al., 1976; Hill et al., 1978).

Giordano et al. (1974) and Kausar et al. (1976) reported a mutual competitive effect of Zn and Cu on absorption by roots. However, in my study, a competition between Cu and Zn probably could not explain the low Cu uptake in the P+Zn treatments because when Zn was added alone, the Cu concentration and uptake was greater than for the P+Zn and the control treatments. There can be several reasons for the lower concentration of Cu in P+Zn treatments than in Zn alone treatments (contrasts). First, the biological dilution effect occurring with applied P might have resulted in the lower Cu concentration in the wheat tissue in the P+Zn treatments than in the Zn alone and the control treatment. In addition, when Zn was added, linear polyphosphates in APP could form soluble Zn complexes leading to less soluble complex formation with native Cu. This could lead to low Cu concentrations and low Cu uptake when Zn was added with APP. However, in DAP+Zn treatments, Cu uptake did not show a decrease as compared to the DAP alone treatment, and this might be due to the high dry matter yield in DAP+Zn treatments. As well, Kurdi and Doner (1983) found a tendency of reduced Cu sorption in soil with high amount of added Zn. Thus under high concentration of added Zn, the soil solution Cu (released from exchangeable sites) may have increased leading to its higher absorption as compared to the control treatment.

The low concentration and uptake of P in APP treatments compared to DAP treatments may be due to the condensed phosphates present in it. Plant uptake of P occurs as primary and secondary orthophosphates, and therefore the condensed P has to be hydrolyzed into orthophosphates (Savant and Racz, 1972). Orthophosphates formed during initial polyphosphate hydrolysis might have retarded the phosphatase activity in soil and hence the subsequent hydrolysis (Savant and Racz, 1972). This could account for the low plant absorption of P with APP treatments in my experiments. Additional studies (Chapter 3 and 5) showed that more APP was sorbed on soil surfaces than DAP, which could result in a lower solution P concentration and lower P absorption. This was confirmed by the low extractable P in APP treatments compared to DAP treatments. In the literature, contradictory results have been reported on the comparative effectiveness of polyphosphate and orthophosphate as a source of P. Rhue et al. (1981) found a lower uptake of P by potato when treated with APP than with DAP. The P uptake by barley was lower when treated with Poly N (a mixture of triammonium pyrophosphate and orthophosphate) as compared to sodium orthophosphate (Mnkeni and MacKenzie, 1988). By contrast, Janssen et al., 1985, and Raun et al., 1987 observed a higher uptake of P by sorghum and corn with the application of polyphosphates than with orthophosphates.

Application of Zn did not decrease the concentration and uptake of Cu by wheat as compared to the control. However, the addition of Cu decreased the concentration and uptake of Zn, which might have resulted from the competitive effect of Cu for the root absorption sites of Zn (Kausar et al., 1976). The increased Zn uptake in P+Zn treatments compared to the Zn alone treatments might be attributed to the beneficial effect of P in increasing the root growth which would enhance Zn uptake.

The DTPA extractable Cu, was higher in APP alone treatments than in DAP alone treatments. This might be due to the solubilization of soil organic matter by the polyphosphates and the release of complexed Cu (Mnkeni and MacKenzie, 1985). Available Cu in soil before wheat growth was 0.35 mg Cu kg soil^{-1} (Table 2.1), which increased to 1.02 mg Cu kg soil^{-1} during the greenhouse experiment in the control treatment. This may be the effect of the rhizosphere on the concentration of available Cu. Without added Cu, there was no relationship between yield of wheat, or uptake of Cu, and the available Cu content in soil. This was in contrast to the findings of Karamanos et al., (1986) who suggested that DTPA-extractable Cu provides an accurate diagnosis of Cu deficiency. However, Marschner (1991) postulated that the role of root surface area and the root-induced changes in the rhizosphere are responsible for the poor correlation between the nutrient availability characterized by chemical extraction methods and the actual nutrient uptake by plants. In addition to the possible rhizosphere effect suggested by Marschner (1991), the acidic pH of my soil sample (5.52) might have affected the DTPA extractable Cu, by decreasing the stability of the DTPA-Cu complex (more stable at pH 7.3 than in acidic pH) formation (Lindsay and Norvell, 1978).

2.5 SUMMARY AND CONCLUSIONS

The experimental soil was deficient in Cu for wheat growth. Copper deficient wheat had visual leaf symptoms, delayed flowering, unfilled grain and partially filled heads. Copper deficiency affected grain yield, but not straw yield at maturity.

Sources of P influenced the yield and the uptake of Cu by wheat. Grain yield was higher in APP treatments than in DAP treatments, when Cu was not added. A greater Cu uptake occurred with the application of APP, with or without added Cu, than with the addition of DAP. However, the P uptake was higher with DAP than with APP application. Zinc added alone increased Cu uptake more than did P+Zn, but the total yield in Zn alone treatment was similar to the control.

In general, Cu deficiency of wheat was overcome by the addition of Cu or APP, but not by DAP or Zn.

Table 2.1 Some characteristics of the soil sample (0-15 cm depth)

Soil subgroup	Eluviated Black Chernozem
Sand	79 %
Silt	7.8 %
Clay	13 %
Soil pH	5.52
Electrical conductance	0.98 dS m^{-1}
Organic carbon	29.3 g kg soil^{-1}
Cation exchange capacity	11.7 c mol (+) kg soil^{-1}
Total P	729 mg P kg soil^{-1}
Total Zn	28.3 mg Zn kg soil^{-1}
Total Cu	5.4 mg Cu kg soil^{-1}
Total Fe	17.5 g kg soil^{-1}
Total Al	35.4 g kg soil^{-1}
†Pyro-Fe	843 mg kg soil^{-1}
‡Ox-Fe	1.66 g kg soil^{-1}
§CBD-Fe	1.80 g kg soil^{-1}
¶Pyro-Al	720 mg kg soil^{-1}
•Ox-Al	776 mg kg soil^{-1}
¥CBD-Al	315 mg kg soil^{-1}
Extractable P	40.5 mg P kg soil^{-1}
Extractable Zn	3.77 mg Zn kg soil^{-1}
Extractable Cu	0.35 mg Cu kg soil^{-1}

---

† Pyrophosphate extractable Fe; ‡ Oxalate extractable Fe; § Citrate-Bicarbonate-Dithionite extractable Fe; ¶ Pyrophosphate extractable Al; • Oxalate extractable Al; ¥ Citrate-Bicarbonate-Dithionite extractable Al

Table 2.2 Influence of incorporated Cu, P and Zn on the yield of total dry matter, straw, grain, and grain to straw ratio at maturity

	Yield			Grain:Straw
Treatments	Total	Straw	Grain	Ratio
	---------------- g plant^{-1} ----------------			
Control	1.91 (0.11)†	1.06 (0.06)	0.84 (0.03)	0.79
APP	2.26 (0.09)	1.20 (0.08)	1.05 (0.03)	0.89
APP+Zn	2.21 (0.21)	1.16 (0.01)	1.04 (0.04)	0.90
APP+Cu	2.54 (0.27)	1.21 (0.02)	1.34 (0.01)	1.11
DAP	1.98 (0.22)	1.21 (0.02)	0.78 (0.12)	0.64
DAP+Zn	2.13 (0.13)	1.19 (0.03)	0.94 (0.03)	0.80
DAP+Cu	2.46 (0.25)	1.20 (0.05)	1.26 (0.02)	1.05
Zn	2.06 (0.15)	1.07 (0.03)	0.99 (0.02)	0.93
Cu	2.27 (0.17)	1.06 (0.04)	1.21 (0.02)	1.15
LSD(0.05)	0.19	NS	0.14	0.17

		Yield		Grain:Straw
Contrasts	Total	Straw	Grain	Ratio
Control vs Others	***	NS	***	**
APP vs DAP	**	NS	***	**
Zn alone Cu alone	**	NS	***	**
P+Zn vs Zn alone	NS	NS	NS	NS
P+Cu vs Cu alone	***	**	NS	NS
‡P alone vs P+Zn /Cu	**	NS	**	***
§APP+Zn /Cu vs DAP+Zn /Cu	NS	NS	NS	NS
P+Zn vs P+Cu	*	NS	***	***

† Standard error of mean (n=3); ANOVA in Appendix 4; * significant at P ≥ 0.05; ** significant at P ≥ 0.01; *** significant at P ≥ 0.001; NS not significant; ‡ P alone vs P+Zn and P+Cu; § APP+Zn and APP+Cu vs DAP+Zn and DAP+Cu

Table 2.3 Influence of incorporated Cu, P and Zn on the mean concentration of Cu, P and Zn in the shoots and their mean total uptake by wheat in a Cu deficient soil (average of four cuts: 20 days, 40 days, 60 days and maturity)

Treatments	Cu		P		Zn	
	Conc. mg Cu kg^{-1}	Total uptake µg Cu plant^{-1}	Conc. g P kg^{-1}	Total uptake mg P plant^{-1}	Conc. mg Zn kg^{-1}	Total uptake µg Zn plant^{-1}
Control	2.58	2.06	2.11	1.86	29.0	32.8
APP	3.02	2.92	2.70	2.52	31.3	40.1
APP+Zn	2.13	2.26	2.65	2.30	47.2	57.7
APP+Cu	5.56	5.70	2.36	2.56	27.0	36.6
DAP	2.13	1.94	3.35	3.08	32.2	37.4
DAP+Zn	2.18	2.06	3.42	3.28	47.2	54.4
DAP+Cu	4.31	4.72	2.87	3.22	25.7	33.7
Zn	3.23	2.92	2.16	2.00	46.5	47.8
Cu	5.20	5.10	1.84	9.26	22.5	26.1

Contrasts	Concentration			Total uptake		
	Cu	P	Zn	Cu	P	Zn
Control vs Others	***	***	***	***	***	***
APP vs DAP	***	***	NS	***	**	**
Zn alone vs Cu alone	***	**	***	***	NS	**
P+Zn vs Zn alone	**	**	NS	**	***	**
P+Cu vs Cu alone	*	***	*	NS	**	NS
‡P alone vs P+Zn /Cu	**	**	**	**	NS	**
§APP+Zn /Cu vs DAP+Zn /Cu	**	***	NS	**	***	**
P+Zn vs P+Cu	***	*	***	***	NS	***

ANOVA for the concentration and total uptake of Cu, P and Zn are given in Appendix 5-10; * significant at $P \geq 0.05$; ** significant at $P \geq 0.01$; *** significant at $P \geq 0.001$; NS not significant; ‡ P alone vs P+Zn and P+Cu; § APP+Zn and APP+Cu vs DAP+Zn and DAP+Cu

Table 2.4 Orthogonal polynomials showing the response of the concentration and uptake of Cu, P and Zn by shoots on harvesting times

	Cu			P			Zn		
Treatments	L†	Q‡	C§	L	Q	C	L	Q	C
Concentration									
Control	***	**	**	***	NS	NS	***	NS	NS
APP	**	**	*	***	***	NS	***	NS	NS
APP+Zn	**	NS	NS	***	**	NS	**	NS	NS
APP+Cu	***	**	**	***	NS	NS	***	NS	NS
DAP	***	NS	NS	***	NS	NS	***	NS	NS
DAP+Zn	NS	NS	NS	***	NS	NS	**	NS	NS
DAP+Cu	**	NS	NS	**	NS	**	***	**	NS
Zn	***	NS	**	**	NS	NS	***	**	NS
Cu	***	**	NS	***	**	NS	*	NS	NS
Uptake									
Control	***	**	**	***	NS	*	***	NS	*
APP	***	**	NS	**	NS	NS	***	NS	**
APP+Zn	***	**	NS	***	NS	NS	***	NS	**
APP+Cu	***	**	NS	***	*	NS	***	NS	***
DAP	***	**	**	***	NS	***	***	**	***
DAP+Zn	***	**	***	***	**	***	***	NS	**
DAP+Cu	**	***	**	**	**	*	**	*	*
Zn	***	**	**	***	NS	**	***	**	***
Cu	***	***	***	***	NS	NS	***	NS	NS

†- Linear response; ‡- Quadratic response; §-Cubic response;

* significant at $P \geq 0.05$; **significant at $P \geq 0.01$; *** significant at $P \geq 0.001$;

NS not significant

Table 2.5 Influence of incorporated Cu, P and Zn on the concentration of Cu, P and Zn in grain in a Cu deficient soil

Treatments	Concentration		
	Cu mg kg^{-1}	P g kg^{-1}	Zn mg kg^{-1}
Control	1.74 (0.09)†	3.47 (0.21)	57.0 (2.96)
APP	1.89 (0.19)	3.49 (0.37)	52.6 (7.85)
APP+Zn	1.66 (0.27)	3.27 (0.17)	64.7 (3.37)
APP+Cu	4.03 (0.28)	2.93 (0.47)	40.7 (2.04)
DAP	1.52 (0.26)	5.66 (0.61)	71.5 (7.23)
DAP+Zn	1.24 (0.04)	4.54 (0.31)	67.7 (2.05)
DAP+Cu	3.40 (0.14)	3.85 (0.12)	38.1 (2.43)
Zn	2.21 (0.06)	3.02 (0.08)	54.3 (4.48)
Cu	4.69 (0.35)	2.93 (0.20)	36.7 (1.85)
LSD (0.05)	0.63	0.77	13.0

Contrasts	Cu	P	Zn
Control vs Others	***	**	**
APP vs DAP	***	***	***
Zn alone vs Cu alone	***	NS	**
P+Zn vs Zn alone	***	**	**
P+Cu vs Cu alone	***	NS	**
‡P alone vs P+Zn /Cu	***	***	**
§APP+Zn /Cu vs DAP+Zn /Cu	**	***	NS
P+Zn vs P+Cu	***	NS	***

† Standard error of mean (n=3); ANOVA in Appendix 11; * significant at $P \geq 0.05$; ** significant at $P \geq 0.01$; *** significant at $P \geq 0.001$; NS not significant;

‡ P alone vs P+Zn and P+Cu; § APP+Zn and APP+Cu vs DAP+Zn and DAP+Cu

Table 2.6 Influence of incorporated Cu, P and Zn on the uptake of Cu, P and Zn by grain in a Cu deficient soil

Treatments	Uptake		
	Cu μg $plant^{-1}$	P mg $plant^{-1}$	Zn μg $plant^{-1}$
Control	1.45 (0.04)†	2.90 (0.14)	47.7 (0.86)
APP	1.99 (0.20)	3.67 (0.07)	55.4 (3.28)
APP+Zn	1.75 (0.33)	3.42 (0.19)	67.5 (1.25)
APP+Cu	5.38 (0.39)	3.91 (0.05)	54.3 (2.77)
DAP	1.17 (0.23)	4.25 (0.27)	53.7 (3.52)
DAP+Zn	1.17 (0.04)	4.27 (0.15)	63.9 (1.85)
DAP+Cu	4.28 (0.17)	4.85 (0.12)	48.1 (3.44)
Zn	2.19 (0.05)	2.99 (0.02)	53.8 (4.67)
Cu	5.68 (0.37)	3.56 (0.20)	44.7 (2.89)
LSD (0.05)	0.73	0.48	11.6

Contrasts	Cu	P	Zn
Control vs Others	***	***	**
APP vs DAP	***	***	NS
Zn alone vs Cu alone	***	**	NS
P+Zn vs Zn alone	*	**	**
P+Cu vs Cu alone	**	***	NS
‡P alone vs P+Zn /Cu	***	NS	NS
§APP+Zn /Cu vs DAP+Zn /Cu	***	***	NS
P+Zn vs P+Cu	***	**	***

† Standard error of mean (n=3); ANOVA in Appendix 12; * significant at $P \geq 0.05$; ** significant at $P \geq 0.01$; *** significant at $P \geq 0.001$; NS not significant; ‡ P alone vs P+Zn and P+Cu; § APP+Zn and APP+Cu vs DAP+Zn and DAP+Cu

Table 2.7 Influence of the incorporated Cu, P and Zn on the concentration of extractable P in soil at different times of harvest

	Extractable P concentration at				
Treatments	20d	40d	60d	Maturity	Mean
	------- mg P kg $soil^{-1}$ -------				
Control	25.8 (0.24)†	33.6 (0.42)	25.9 (3.11)	30.4 (0.38)	28.9
APP	38.1 (6.63)	44.1 (0.55)	39.4 (1.55)	41.9 (0.55)	40.9
APP+Zn	50.8 (1.58)	43.9 (1.57)	36.1 (2.18)	43.5 (0.77)	43.6
APP+Cu	54.0 (0.22)	44.8 (0.78)	33.0 (1.27)	40.8 (1.89)	43.2
DAP	68.0 (2.47)	58.6 (0.76)	46.5 (2.49)	51.2 (0.94)	56.1
DAP+Zn	71.3 (0.63)	59.5 (0.51)	49.8 (1.80)	51.8 (0.66)	58.1
DAP+Cu	71.4 (0.87)	59.1 (0.30)	44.1 (2.63)	51.5 (0.50)	56.5
Zn	38.1 (0.47)	33.8 (0.03)	28.8 (1.42)	30.2 (0.59)	32.7
Cu	37.3 (0.54)	33.4 (0.25)	26.6 (2.63)	28.5 (0.90)	31.4
LSD (0.05)	7.3	2.1	6.6	2.7	
Contrasts					
Control vs Others		***			
APP vs DAP		***			
Zn alone vs Cu alone		NS			
P+Zn vs Zn alone		***			
P+Cu vs Cu alone		***			
‡P alone vs P+Zn /Cu		**			
§APP+Zn /Cu vs DAP+Zn /Cu		***			
P+Zn vs P+Cu		NS			

† Standard error of mean (n=3); ANOVA is given in Appendix 13;

** significant at $P \geq 0.01$; *** significant at $P \geq 0.001$; NS not significant;

‡ P alone vs P+Zn and P+Cu; § APP+Zn and APP+Cu vs DAP+Zn and DAP+Cu

Table 2.8 Orthogonal polynomials showing the response of the concentration of extractable P, Cu and Zn in soil to harvesting time

	P			Cu			Zn		
Treatments	L†	Q‡	C§	L	Q	C	L	Q	C
Control	NS	NS	***	***	***	NS	NS	NS	***
APP	NS	NS	**	NS	NS	NS	***	**	*
APP+Zn	***	***	*	***	**	***	NS	***	**
APP+Cu	***	***	**	**	NS	NS	***	***	**
DAP	***	***	**	NS	**	NS	***	NS	NS
DAP+Zn	***	***	NS	***	*	NS	**	***	NS
DAP+Cu	***	***	***	NS	**	NS	**	*	NS
Zn	***	NS	NS	**	***	NS	***	NS	NS
Cu	**	NS	NS	NS	**	NS	***	***	***

† Linear response; ‡ Quadratic response; § Cubic response;

* significant at $P \geq 0.05$; **significant at $P \geq 0.01$; *** significant at $P \geq 0.001$;

NS not significant

Table 2.9 Influence of incorporated Cu, P and Zn on the concentration of DTPA extractable Cu in soil at different times of harvest

	Concentration of Cu at				
Treatments	20d	40d	60d	Maturity	Mean
	mg Cu kg soil^{-1}				
Control	1.15 (0.09)†	0.54 (0.00)	1.32 (0.08)	1.05 (0.01)	1.02
APP	1.15 (0.09)	0.63 (0.02)	1.02 (0.03)	0.92 (0.00)	0.93
APP+Zn	1.01 (0.04)	0.48 (0.03)	0.81 (0.02)	0.94 (0.00)	0.81
APP+Cu	5.46 (0.18)	5.91 (0.13)	5.81 (0.05)	4.38 (0.34)	5.39
DAP	0.44 (0.04)	0.45 (0.01)	0.58 (0.04)	0.94 (0.00)	0.60
DAP+Zn	0.69 (0.07)	0.44 (0.02)	0.61 (0.00)	0.95 (0.00)	0.67
DAP+Cu	5.58 (0.11)	5.93 (0.17)	5.41 (0.18)	4.14 (0.06)	5.27
Zn	0.65 (0.10)	0.48 (0.02)	0.77 (0.08)	1.00 (0.04)	0.73
Cu	5.44 (0.15)	6.02 (0.29)	5.78 (0.11)	3.79 (0.26)	5.26
LSD (0.05)	0.41	0.36	0.36	0.28	

Contrasts	
Control vs Others	***
APP vs DAP	***
Zn alone vs Cu alone	***
P+Zn vs Zn alone	NS
P+Cu vs Cu alone	NS
‡P alone vs P+Zn /Cu	***
§APP+Zn /Cu vs DAP+Zn /Cu	**
P+Zn vs P+Cu	***

---

† Standard error of mean (n=3); ANOVA is given in Appendix 13;
** significant at $P \geq 0.01$; *** significant at $P \geq 0.001$; NS not significant;
‡ P alone vs P+Zn and P+Cu; § APP+Zn and APP+Cu vs DAP+Zn and DAP+Cu

Table 2.10 Influence of incorporated Cu, P and Zn on the concentration of DTPA extractable Zn in soil at different times of harvest

Treatments	Concentration of Zn at				
	20d	40d	60d	Maturity	Mean
	mg Zn kg soil^{-1}				
Control	2.86(0.17)†	4.55 (0.06)	4.49 (0.16)	3.89 (0.07)	3.95
APP	3.85 (0.08)	4.30 (0.13)	3.94 (0.11)	3.85 (0.02)	3.99
APP+Zn	13.5 (0.14)	16.0(0.02)	13.7 (0.33)	11.4 (0.11)	13.7
APP+Cu	4.32 (0.12)	4.37 (0.16)	4.00 (0.02)	3.63 (0.04)	4.08
DAP	3.63 (0.12)	4.29 (0.01)	3.91 (0.06)	3.47 (0.03)	3.83
DAP+Zn	13.0 (0.05)	14.8 (0.31)	13.3 (0.10)	10.4 (0.21)	12.9
DAP+Cu	3.67 (0.14)	4.18 (0.11)	3.96 (0.07)	3.27 (0.02)	3.77
Zn	13.6 (0.14)	15.7 (0.04)	13.7 (0.18)	9.53 (1.09)	13.1
Cu	3.53 (0.08)	4.38 (0.08)	4.15 (0.23)	3.34 (0.10)	3.85
LSD(0.05)	0.35	0.40	0.51	1.12	

Contrasts	
Control vs Others	***
APP vs DAP	***
Zn alone Cu alone	**
P+Zn vs Zn alone	NS
P+Cu vs Cu alone	NS
‡P alone vs P+Zn /Cu	***
§APP+Zn /Cu vs DAP+Zn /Cu	***
P+Zn vs P+Cu	**

---

† Standard error of mean (n=3); ANOVA is given in Appendix 13;
** significant at $P \geq 0.01$; *** significant at $P \geq 0.001$; NS not significant;
‡ P alone vs P+Zn and P+Cu; § APP+Zn and APP+Cu vs DAP+Zn and DAP+Cu

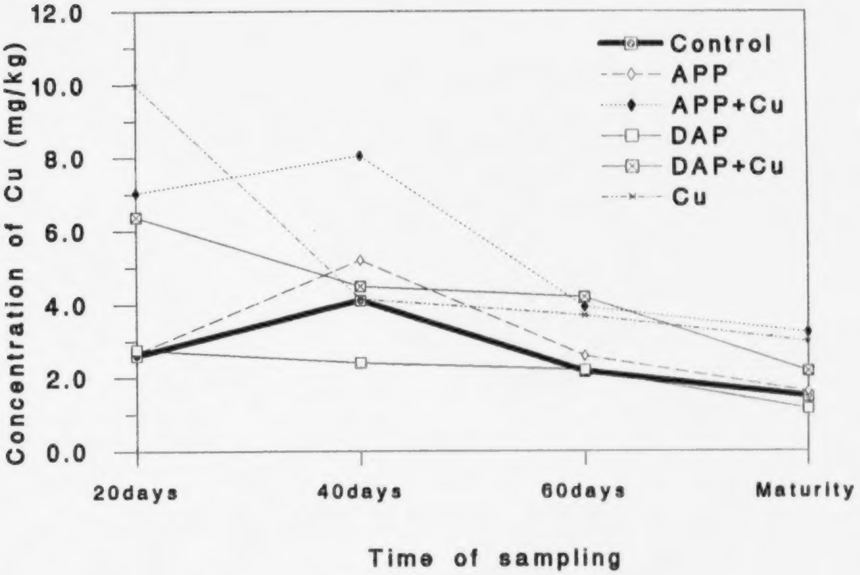


Fig. 2.1 Influence of APP and DAP on the concentration of Cu in wheat shoots at different times of harvest (LSD values for comparing treatments at four sampling times are 1.4, 0.6, 0.5 and 0.4 respectively; Each point is a mean of three replications)

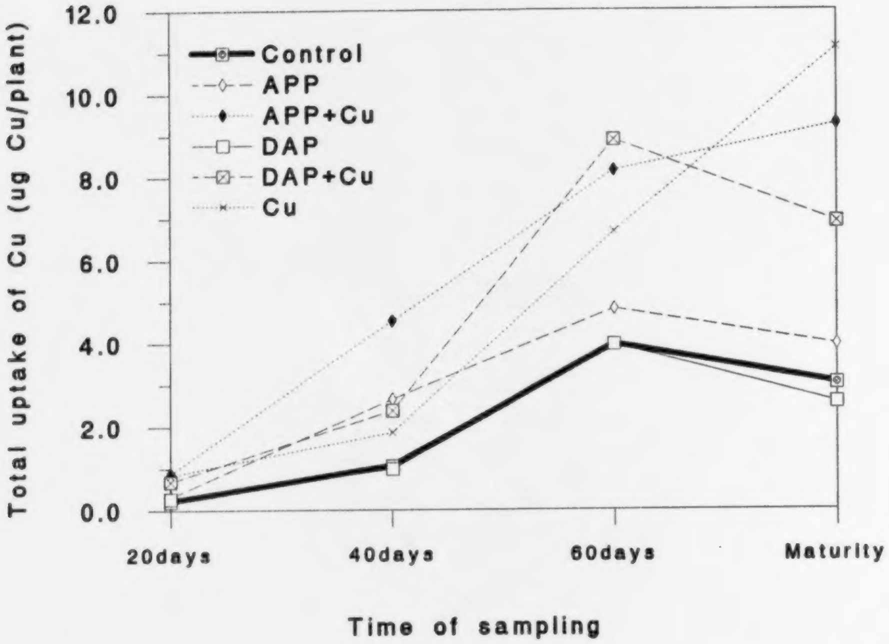


Fig. 2.2 Influence of APP and DAP on the total uptake of Cu by wheat at different times of harvest (LSD values for comparing treatments at four sampling times are 0.14, 0.30, 1.01 and 2.19 respectively; Each point is a mean of three replications)

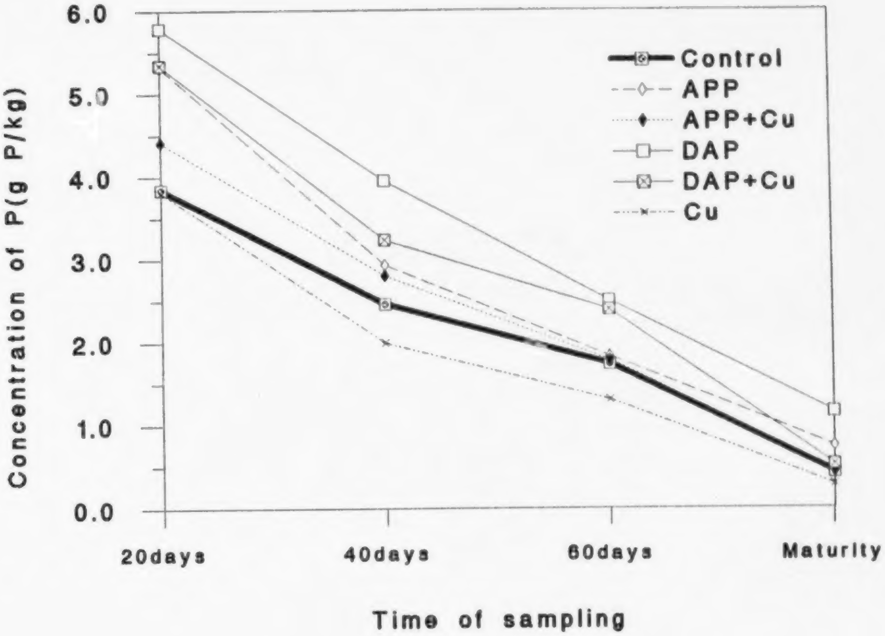


Fig. 2.3 Influence of APP and DAP on the concentration P in wheat shoots at different times of harvest (LSD values for comparing treatments at four sampling times are 0.62, 0.34, 0.59 and 0.30 respectively; Each point is a mean of three replications)

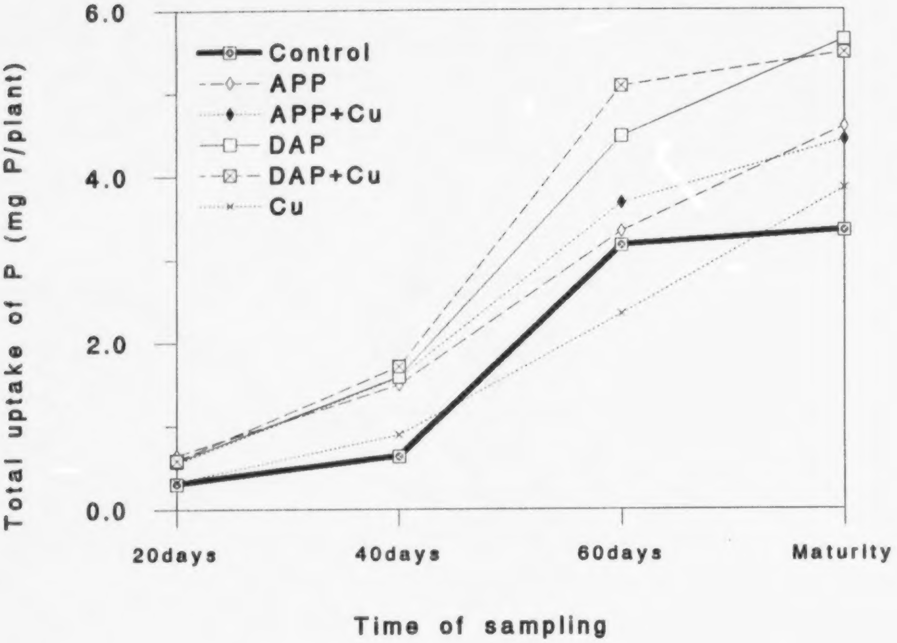


Fig. 2.4 Influence of APP and DAP on the total uptake of P by wheat at different times of harvest (LSD values for comparing treatments at four sampling times are 0.12, 0.35, 1.10 and 0.53 respectively; Each point is a mean of three replications)

2.6 REFERENCES

Asher L.E., and B.Bar-Yosef. 1982. Effects of pyrophosphate, EDTA and DTPA on zinc sorption by montmorillonite. Soil Sci. Soc. Am. J. 46: 271-276

Bingham, F. T., J. P. Martin, and J. A. Chastain. 1958. Effects of phosphorus fertilization of California soils on minor element nutrition of citrus. Soil Sci. 86: 24-31.

Bingham, F. T., and M. J. Garber. 1960. Solubility and availability of micronutrients in relation to P fertilization. Soil Sci. Soc. Am. Proc. 24: 209-213.

Corbridge, D.E.C. 1985. phosphorus: An outline of its chemistry, biochemistry and technology. 3rd ed. Elsevier Sci. Publishers,New York.

Dell B. 1981. Male sterility and wall structure in copper deficient plants. Ann. Bot. 48: 599-608.

Dick R.P. and M.A.Tabatabai. 1987. Polyphosphates as sources of phosphorus for plants. Fert. Res. 12: 107-108.

Dudas, M. J. and S. Pawluk. 1980. Natural abundances and mineralogical partitioning of trace elements in selected Alberta soils. Can. J. Soil Sci. 60: 763-771.

Gee, G. W., and J. W. Bauder. 1986. Particle-size analysis. *In* A. Klute (ed.) Methods of soil analysis. Part 1- Physical and mineralogical methods. American Soc. Agron. 9: 383-409.

Giordano, P. M. and J. J. Mortvedt. 1969. Phosphorus availability to corn as affected by granulating Mn with ortho and pyrophosphate fertilizers. Proc. Soil Sci. Soc. Am. 33: 460-463.

Giordano P.M., J.C. Noggle, and J.J. Mortvedt. 1974. Zinc uptake by rice as affected by metabolic inhibitors and competing cations. Plant Soil . 41: 637-646.

Graham R.D. 1975. Male sterility in wheat plants deficient in copper. Nature. 254: 514-515.

Hashimoto I., J. D. Hughes, and O.D. Philen. 1969. Reactions of triammonium pyrophosphate with soils and soil minerals. Proc. Soil Sci. Soc. Am. 33: 401-405.

Hashimoto I. and Z.T. Wakefield. 1974. Hydrolysis of pyrophosphate in soils. Response to temperature and effect on heavy metal uptake by plants. Soil Sci. 118: 90-94.

Hill J., A.D. Robson, and J.F. Loneragan. 1978. The effect of copper and nitrogen supply on the translocation of copper in four cultivars of wheat. Aust. J. Agric. Res. 29: 925-939.

Huheey, J.E. 1972. Inorganic Chemistry: Principles of structure and reactivity. Harper and Row, New York.

Janssen, K. A., D. A. Whitney, and D. E. Kissel. 1985. Phosphorus application frequency and sources for grain sorghum. Soil Sci. Soc. Am. J. 49: 754-757.

Karamanos, R. E., G. A. Kruger, and J. W. B. Stewart. 1986. Cu deficiency in cereal and oilseed crops in northern Canadian prairie soils. Agron. J. 78: 317-323.

Kausar M. A., F.M. Chaudhry, A. Rashid , A. Latif, and S.M. Alam. 1976. Micronutrient availability to cereals from calcareous soils.I. Comparative Zn and Cu deficiency and their mutual interaction in rice and wheat. Plant Soil. 45: 397-410.

Khasawneh F.E., E.C. Sample, and I. Hashimoto. 1974. Reactions of ammonium ortho and polyphosphate fertilizers in soil. 1. Mobility of phosphorus. Proc. Soil Sci. Soc. Am. 38: 446-450.

Kinniburgh, D. G., M. L. Jackson, and J. K. Syers. 1976. Adsorption of alkaline earth, transition, and heavy metal cations by hydrous oxide gels of iron and aluminum. Soil Sci. Soc. Am. J. 40: 796-799.

Kruger, G. A., R. E. Karamanos, and J. P. Singh. 1985. The Cu fertility of Saskatchewan soils. Can. J. Soil Sci. 65: 89-99

Kurdi, F. and H. E. Doner. 1983. Zn and Cu sorption and interaction in soils. Soil Sci. Soc. Am. J. 47: 873-876.

Lindsay, W. L. and W. A. Norvell. 1978. Development of a DTPA soil test for Zn, Fe, Mn and Cu. Soil Sci. Soc. Am. J. 42: 421-428.

Loneragan J.F., K. Snowball, and A.D. Bobson. 1976. Remobilization of nutrients and its significance in plant nutrition. p 463-469. *In* Wardlaw I.F. and J.B.

Passioura (ed.) Transport and transfer process in plants. Academic Press, London.

Malhi, S. S., L. J. Piening, and D. J. MacPherson. 1987. Effect of Cu on stem melanosis of Park wheat. p. 142-148. *In* Proc. of the 24th Annual Alberta Soil Sci. Workshop. Calgary, Alberta. Feb. 17-18.

Marschner H. 1991. Root- induced changes in the availability of micronutrients in the rhizosphere.p. 503-528. *In* Waisel Y., A.Eshel , and U. Kafkafi. Plant root: the hidden half . Marcel Dekker Inc. N.Y.

McKeague, J.A. 1978. Manual on soil sampling and methods of analysis. Canada Soil Survey Committee. Can. Soc. Soil Sci.

McLaren, R.G., and D. V. Crawford. 1973. Studies on soil copper. II. The specific adsorption of Cu by soils. J. Soil Sci. 24: 443-452.

Miller, J.R. and J.H. Axley. 1956. Correlation of chemical soil tests for available phosphorus with crop response, including a proposed method. Soil Sci. 82: 117-127

Mnkeni P.N.S. and A.F. MacKenzie. 1985. Retention of ortho- and polyphosphates in some Quebec soils as affected by added organic residues and calcium carbonate. Can. J. Soil Sci. 65: 575-585.

Mnkeni P.N.S. and A.F. MacKenzie. 1988. Ortho- and polyphosphate P fertilizers as affected by added organic materials and calcium carbonate. Can. J. Soil Sci. 68: 243-250.

Mortvedt J.J. and P.M. Giordano. 1967. Zinc movement in soil from fertilizer granules. Proc. Soil Sci. Soc. Am. 31: 608-613.

Mortvedt J.J. and P.M. Giordano. 1969. Availability to corn of zinc applied with various macronutrient fertilizers. Soil Sci. 108: 180-187.

Mortvedt J.J. and P.M. Giordano. 1975. Crop response to manganese sources applied with ortho and polyphosphate fertilizers. Proc. Soil Sci. Soc. Am. 39: 782-784.

Nambiar , E.K.S. 1976. Genetic difference in Cu nutrition of cereals.1.differential responses of genotypes to copper. Aust. J. Agric Res. 27: 453-463.

Nelson, D.W. and L.E. Sommers. 1982. Total C, organic C and organic matter. p.

539-579 *In* Page, A.L., R.H. Miller and D.R. Keeney(ed.) Methods of soil analysis. Part 2. Chemical and microbiological properties Am. Soc. Agron. Monograph No.9 (2nd Ed.) Madison, Wisconsin

Penney D.C, E.D. Solberg, and I.R. Evans. 1988. The Cu fertility of Alberta soils. p . 125-133. *In* Proc. of 25th Annual Alberta Soil Sci. Workshop. Lethbridge, Alberta, Feb. 23-24, 1988.

Piening, L. J., D. J. MacPherson, and S. S. Malhi. 1989. Stem melanosis of some wheat, barley, and oat cultivars on a Cu deficient soil. Can. J. Plant Pathology 11: 65-67

Raun W. R., D.H. Sander, and R.A. Olson. 1987. Phosphorus fertilizer carriers and their placement for minimum till corn under sprinkler irrigation. Soil Sci. Soc. Am. J. 51: 1055-1062.

Rhue, R. D., D. R. Hensel, T. L. Yuan, and W. K. Robertson. 1981. Ammonium orthophosphate and ammonium polyphosphate as sources of P for potatoes. Soil Sci. Soc. Am. J. 45:1229-1231.

SAS Institute Inc. 1987. SAS/STAT Guide for personal computers, Version 6 Edition, Cary, N.C: SAS Institute Inc.

Savant N. K. and G.J. Racz. 1972. Hydrolysis of sodium pyrophosphate and tripolyphosphate by plant roots. Soil Sci. 113: 18-22.

Schindler, P. W., B. Furst, R. Dick, and P. U. Wolf. 1976. Ligand properties of surface silanol groups: I. Surface complex formation with Fe^{3+}, Cu^{2+}, Cd^{2+}, and Pb^{2+}. J. Colloid Interface Sci. 55: 469-475.

Schnitzer M and P. Schuppli. 1989. The extraction of organic matter from selected soils and particle size fractions with 0.5M NaOH and 0.1 M $Na_4P_2O_7$ solutions. Can. J. Soil Sci. 69: 253-262.

Showk, A.A.M., R. L. Westerman, and D.L. Weeks. 1987. Influence of P sources and rates on soil pH, extractable P and DTPA extractable micronutrients. Soil Sci. 144: 36-42.

Soon, Y. K., and S. Abboud. 1990. Trace elements in agricultural soils of northwestern Alberta. Can. J. Soil Sci. 70: 270-288.

White M.C., F.D. Baker, R. L.Chaney, and A.M. Decker. 1981. Metal complexation in xylem fluid II. Theoretical equilibrium model and computational computer programme. Plant Physiol. 67: 301-310.

White, R.T., and G. E. Douthit. 1985. Use of microwave oven and nitric acid-hydrogen peroxide digestion to prepare botanical materials for elemental analysis by Inductively Coupled Argon Plasma Emission Spectroscopy. J. Assoc. Off. Anal. Chem. 68: 766-769.

Chapter 3

IMMEDIATE INFLUENCE OF SORBED PHOSPHATES ON THE SORPTION-DESORPTION REACTIONS OF Cu

3.1 INTRODUCTION

Sorption-desorption reactions are important in the partitioning of a particular solute between soil solids and the soil solution. Consequently, these reactions are of interest in plant nutrition and environmental studies. Adsorbed P changes the surface characteristics of the adsorbents (Gillman and Fox, 1980; Kuo and McNeal, 1984). For example, sorption of P increased the number of specific sorption sites for Zn, and sorbed Zn was not readily displaced by other cations (Neilsen et al., 1986; Xie and MacKenzie, 1989). The availability of favourable nucleation sites on surfaces of the adsorbents influences the sorption and the subsequent desorption of metals. By influencing the nature of the surface nucleation sites, different forms of added P may affect the sorption-desorption of Cu, but no work has been reported previously.

Desorption of sorbed cations is influenced by the enthalpy of adsorption and the rate of metal loading (McBride, 1978; Boyd et al., 1981). Copper adsorbed at low site coverage was bound more strongly than Cu adsorbed when a large portion of available sites was occupied (McLaren and Crawford, 1973). A portion of the Cu sorbed in a gibbsite suspension was not rapidly reversible (McBride et al., 1984). Studies of Pb adsorption and desorption by goethite suspensions indicated that the adsorption reaction step is fast, whereas desorption is much slower, and probably limited by the activation energy required to break the Pb surface bonds (Hayes and Leckie, 1986). In the field, crops depend on the ions desorbed from the solid phase and so knowledge of the characteristics of desorption is important for assessing the factors that control the utilization of fertilizers (Lemare and Leon, 1989).

Ammonium polyphosphate contains orthophosphate and a mixture of linear condensed phosphates including pyrophosphate. The chemical behaviour of linear phosphates depends on their chain lengths. The products of polyphosphate hydrolysis have different chain lengths, with the ultimate products being orthophosphate (Blanchar and Hossner, 1969a; Corbridge, 1985; Dick and Tabatabai, 1986). Hence the sorption reactions of polyphosphates can change with time, and also the sorption behaviour is different from that of orthophosphates (Hashimoto et al., 1969; Blanchar and Hossner, 1969b; Al-Kanani and MacKenzie, 1991). These reactions of the added P, may influence the sorption reactions of the subsequently added metals. In addition to the influence on the surface reactions, pyrophosphates are reported to complex trace elements in soil solution (Bar-Yosef and Asher, 1983).

Sorption-desorption reactions of Cu may be dependent on the availability of suitable nucleation sites, and the orientation of the molecules already on the adsorbing surface affects the arrangement of nucleation sites. For example, different P compounds having different structures, may have different orientation on the surfaces. This could influence the sorption reaction of subsequently added Cu. Studies have shown that reactions of Zn in autoclaved soils differed with prior treatment with orthophosphate and pyrophosphate (Xie and MacKenzie, 1990), but the sorption-desorption reactions of Cu have not been documented on pure mineral or soil surfaces when polyphosphate has been previously sorbed on those surfaces. Therefore the objective of this experiment was to find the immediate influence of the sorption of orthophosphate and polyphosphate, applied at different concentrations, on the sorption-desorption reactions of subsequently added Cu in a Cu deficient soil.

3.2 MATERIALS AND METHODS

The Cu deficient soil studied in the greenhouse experiment (Chapter 2) was used. Some of the properties of the experimental soil are given in Table 2.1. The air dried sample was sieved to ≤ 1 mm. Sorption and desorption of P and Cu were carried out by three sequential equilibrium extractions with: 1) orthophosphate or polyphosphate in 0.03M $KClO_4$; 2) Cu in 0.03M $KClO_4$; and 3) only 0.03 M $KClO_4$ solutions. Phosphorus was added at 0, 25, 50 and 75 μmol P g soil^{-1} as either ammonium polyphosphate (APP) or diammonium orthophosphate (DAP) and Cu at 0, 3, 6, 9, 12 and 15 μmol Cu g soil^{-1}

as $CuSO_4.5H_2O$. Phosphorus pretreatments at each concentration of Cu (for Cu sorption isotherm) were: Control (No P), APP25, APP50, APP75, DAP25, DAP50 and DAP75. There were two replications with 14 experimental units at each Cu concentration. Potassium perchlorate was used as the background electrolyte because of its weak complex formation. The solution pH was adjusted to 5.80 ± 0.02 using dilute KOH or $HClO_4$.

Soil samples (3g) were equilibrated with 30 mL of the P solutions of different concentrations on a reciprocating shaker. After equilibration, samples were centrifuged, and the supernatant removed for the estimation of total P. The residue after the P pretreatment was then equilibrated with 30 mL of the Cu solutions of various concentrations. The suspension was centrifuged and the supernatant removed for the estimation of Cu concentration. Finally, 30 mL of 0.03 M $KClO_4$ solution without P or Cu was added to the residue, equilibrated, centrifuged and the supernatant removed for determining desorbed Cu and P. The pH values of the suspensions were adjusted to 5.80 ± 0.02 after each solution addition. All the equilibrations were for 48 hours and centrifugation for 20 minutes at 22000 RPM.

The first equilibration was for P sorption, the second for Cu sorption and P desorption, and the third for Cu desorption and the remaining P desorption. Corrections were made for the interstitial P or Cu carried over from the previous equilibrations. Total P and Cu (ionic and complexed) in the supernatant solution after centrifugation were determined by the Inductively Coupled Plasma Atomic Emission Spectroscopy. Sorbed P and Cu were calculated from the initial and the final equilibrium solution concentrations. Based on R^2 values, the Freundlich adsorption isotherm equation was selected over the Langmuir equation to depict the Cu sorption reaction. The equation takes the form:

$$q = K\, C^{(1/n)}$$ where

q is the amount of Cu sorbed (μmol Cu g soil^{-1})

C is the equilibrium concentration of Cu (μmol Cu mL^{-1})

K and n are constants

The partition coefficient (Kd) was calculated as the ratio of the sorbed Cu or P to their final solution concentrations.

Statistical analysis

Analysis of variance at each concentration of added Cu (14 experimental units), and over all Cu concentrations (84 experimental units) was done for sorbed Cu, desorbed Cu and P using PROC GLM in SAS (SAS Institute, 1987). Homogeneity of error variance was tested by plotting the residuals against the predicted values using PROC PLOT, and the normality of error was tested using PROC UNIVARIATE. Contrasts were used for comparing the P sources and their concentrations with respect to the amount of Cu sorbed and that is desorbed. Orthogonal polynomials were used to find the relationship between the amounts of P application and the sorbed P, sorbed Cu, desorbed Cu, and desorbed P. Comparisons of individual P pretreatments at each Cu concentrations were made using LSD because of the nonfactorial nature of the experiment (only one control treatment for APP and DAP). Parameters of the Freundlich adsorption isotherm equation were calculated with PROC NLIN (Appendix 16), and PROC GPLOT was used for generating the graphs.

3.3 RESULTS AND DISCUSSION

3.3.1 SORPTION OF P

Various pretreatments affected the amount of sorbed P (Appendix 14). Addition of APP resulted in a higher sorption of P at all amounts compared to DAP, and the absolute differences increased with the quantity of added P (Table 3.1). The equilibrium solution concentrations of P when APP was added at 25, 50 and 75 μmol P g soil^{-1}, were 1.8, 3.8 and 6.1 μmol P mL^{-1}, respectively (Table 3.1). The corresponding values when DAP was added were 2.8, 5.9 and 10 μmol P mL^{-1} respectively. These results of higher sorption of polyphosphates than orthophosphates are comparable with those reported by Sutton and Larsen (1964); Blanchar and Hossner (1969b), and Xie and MacKenzie (1990). Sorbed P increased quadratically with the amount of added P.

The experimental soil was low in clay content. The possible chemisorption sites for P are the broken edges of phyllosilicates and the amorphous Fe and Al oxides. Since the P sorption was done using the whole soil, identification of the specific sorption sites was not possible. However, free Fe and Al oxide (nonsilicate Fe and Al) content of soil was high (Table 2.1), and they might have provided high affinity sites (high affinity sites refers to chemisorption sites where a bidentate mechanism operates) for P sorption. These sorbing components have heterogeneous adsorption sites (McLaren and Crawford, 1973; Sayin et al., 1990). The higher sorption of APP than DAP might be related to the difference in their structure. In a polyphosphate chain, a wide range of P-O-P angles with high rotational flexibility is found, and polyphosphates are not specific to the coordination requirements of particular cations (Corbridge, 1985). This may enable the added polyphosphate chain to coordinate with the metallic cations (mainly Fe and Al in my soil) found on the solid surface even in the absence of a continuous array of sorption sites, resulting in a greater sorption than with DAP. On the other hand the unhooked single tetrahedron in DAP can coordinate only with adsorbing sites with certain specifications.

The partition coefficient (Kd) decreased with increasing quantity of added P and it was higher for APP compared to DAP at each amount of application (Table 3.1). There was a quadratic decrease in Kd with the amount of added P. There are two probable explanations for the decrease in Kd with increasing quantity of added P. First, when P is added, the adsorbing sites with greater bonding energy will be filled before other sites. As the quantity of added P increases, the adsorbing sites with lower affinity will also be occupied depending on the competing ions. The relatively high Kd at lower concentration of added phosphates indicates that the added P at lower concentration was sorbed to the surface with greater affinity than that added at higher concentration. Secondly, organic anions produced by the solubilization of organic matter might have increased with the quantity of added P, particularly in the presence of polyphosphates (Giordano et al., 1971: Mortvedt and Osborn, 1977; Mnkeni and MacKenzie, 1985). These organic anions may compete with phosphate for sorbing sites resulting in a lower P sorption (Sibanda and Young, 1986; Eze and Loganathan, 1990). The higher value of Kd for APP is a reflection of the greater affinity of the polyphosphate chain for the soil surface compared to the individual tetrahedron of orthophosphate.

3.3.2 SORPTION OF Cu

More than 90 per cent of the added Cu was sorbed in all the treatments (Table 3.2). This pattern is consistent with other results for Cu sorption at similar pH values (McLaren et al., 1981). The amount of sorbed Cu varied with the form and concentrations of added P (Fig. 3.1-3.3, and Table 3.2). The sorption of Cu was greater where the soil was pretreated with DAP, compared to APP (contrasts). Bolland et al. (1977) also observed an increase in the sorption of Zn in the presence of orthophosphate. However my results contradict the work of McBride (1985a) who reported a decrease in the sorption of Cu in the presence of the previously added orthophosphate. Addition of APP at the highest concentration resulted in a lower Cu sorption compared to its addition at 25 and 50 μmol P g $soil^{-1}$. In the case of DAP, the lowest mean sorption of Cu (average of all concentrations) occurred when P was at 25 μmol P g $soil^{-1}$. The difference between APP and DAP with respect to the sorbed Cu increased with the concentration of added Cu (Table 3.2). In both forms of P, there was a linear or quadratic relationship between the increase in the concentration of P, and the amount of Cu sorbed.

The amount of Cu in equilibrium solution was substantially higher in APP pretreated soil than in DAP pretreated soil for a given Cu addition. For example, at an added concentration of 9 μmol Cu g $soil^{-1}$, the solution concentration of Cu in APP75 treatment was 0.54 μmol Cu mL^{-1} (9.00 - 8.46) as against 0.22 μmol Cu mL^{-1} (9.00 - 8.78) in DAP75 treatment (Table 3.2). The increased sorption of Cu following orthophosphate pretreatments as compared to polyphosphate pretreatments, contrasts with the results of Xie and MacKenzie (1990) for the sorption of Zn in some of the autoclaved soils of Quebec. However, Bar-Yosef and Asher (1983) noted a lower sorption of Zn in the presence of polyphosphate.

The partition coefficient of Cu was higher when pretreatment was with orthophosphate compared to polyphosphate (Table 3.3; contrasts). The Kd of Cu decreased linearly with increasing sorption of P as polyphosphate, but quadratically with orthophosphate (orthogonal polynomials). The change in the Kd of Cu with increasing concentration of added Cu was greater when the form of pretreatment was orthophosphate compared to polyphosphate. The higher Kd of Cu after pretreatment with DAP was an indication of the greater affinity of the orthophosphated surface for Cu compared to the APP pretreated surface.

The shape of the Cu sorption isotherm changed with the concentration of added phosphates. The L-type (Langmuir curve) sorption isotherm was observed in the control and when APP and DAP were added at 25 μmol P g soil^{-1} (Fig. 3.1). Harter (1983), Msaky and Calvet (1990) also observed L-type sorption isotherm for Cu sorption by soils under similar pH values. This type of sorption isotherm indicates high affinity of the adsorbing surface for Cu at low concentration coupled with a decreasing amount of the adsorbing surface as the concentration of Cu increased (Msaky and Calvet, 1990). In the above treatments, the Kd of Cu decreased with increasing concentration of added Cu (Table 3.3). Soil pretreated with APP at 50 and 75 μmol P g soil^{-1} tended to have a C-type (constant partition) Cu sorption isotherms (Fig. 3.2-3.3) as shown by the nearly constant Kd value.

When the quantity of the added DAP was 50 μmol P g soil^{-1}, the Cu sorption isotherm tended to have a H-curve (Fig.3.2). H-type isotherm for Cu sorption was also reported by Harter (1983). This H-curve (high affinity curve) is an indication of the high relative affinity of the solid phase for Cu, and is supported by the high Kd values (Table 3.3). This condition is usually produced by highly specific interactions between the solid phase and the adsorbing substance. In this case the divalent Cu could act as a bridging cation for the two adjacently sorbed HPO_4^{2-} and/or the partially hydrolyzed $Cu(OH)^+$ could get bonded to the surface by a unidentate mechanism.

The shape of the Cu sorption isotherm changed to S- curve (sigmoid curve) when the initial application of DAP was 75 μmol P g soil^{-1} (Fig.3.3). These samples showed an increase in the Kd value for Cu sorption with a rise in the concentration of added Cu. The initial low Kd value could be the result of the formation of the nonadsorbing complexes of Cu with the organic compounds in the soil solution. After the complexing capacity of these organic compounds was exceeded through an increase in the amount of added Cu to the soil solution, the phosphated surface began to adsorb Cu ions.

The low Cu sorption in the presence of APP could arise from several mechanisms. First, the direct soluble complex formation of Cu by the condensed phosphates at high concentration (Lindsay et al., 1962; Asher and Bar-Yosef, 1982, and Bar-Yosef and Asher, 1983; Corbridge, 1985). Secondly, the high concentration of organic ligands in the presence of APP is expected to form soluble complexes with Cu, resulting in its low sorption (McLaren et al., 1981). The metal/ligand ratio is critical in determining whether metal adsorption at a surface is enhanced or inhibited, because a large excess of ligands in solution shifts the equilibrium in favour of soluble metal complexes (McBride, 1985b). With DAP, the concentration of organic anions released would be low relative to APP. These organic anions at low concentration in the presence of DAP may have formed ternary complexes with the phosphated surface (Davis and Leckie, 1978; Elliot and Huang, 1980, 1981) leading to high Cu sorption. Thirdly, the initial high sorption of polyphosphate chains may act as a physical barrier for the subsequent sorption of Cu. By contrast, sorption of single phosphate tetrahedra on an isolated sorbing surface could increase the Cu sorption where Cu act as a bridging cation between adjacent orthophosphates or Cu gets sorbed directly on the uncovered sorbing surface in soil.

3.3.3 DESORPTION OF Cu AND P

The effect of pretreatment with phosphates on the desorption of native and added Cu was different (Table 3.4). The amount of desorbed native Cu (measured from treatments without any addition of Cu) tended to be more in the pretreated sample than in the control, and the extent of desorption increased with the concentration of added APP, but not with DAP. No comparable studies have been reported in the literature.

The increased desorption of native Cu after P pretreatment, particularly with polyphosphate, might have resulted from solubilization of soil organic matter and the consequent release of the bound Cu (McLaren and Crawford, 1973; Gregor and Powell, 1986). The effect of polyphosphate in increasing the desorption of native Cu is also evident from the increased desorption with its (APP) increasing quantity (Fig.3.4-3.6). The desorption of native Cu decreased with pretreatment with DAP, and this could be the result of the precipitation or occlusion of the Cu sorbed surface by the orthophosphate anion.

Desorption of the sorbed Cu was not complete in 48 hours. Desorption of the sorbed Cu was influenced by P pretreatments and the concentration of added Cu. The desorbed Cu represented the portion of the sorbed Cu that was held by nonspecific sorption mechanism (on exchange sites), because the desorption was done by $KClO_4$ where K^+ had lower affinity for sorption sites than Cu^{2+}. This may be the reason for the low desorption of the sorbed Cu. Similar observations of low desorption of Cu with weak electrolytes were made by McLaren et al., 1983. Maximum desorption of sorbed Cu was from the non-phosphated pretreatment suggesting different sorption energy on the nonphosphated and the phosphated soil surfaces (Table 3.4; Fig. 3.4-3.6). The proportion of the sorbed Cu which was subsequently desorbed decreased with increasing concentration of added P. There was a quadratic decrease in the desorbed Cu with increasing amounts added APP and DAP. Following pretreatment with polyphosphate, a larger portion of the sorbed Cu was desorbed than when the soil was pretreated with DAP (contrasts). The influence of increasing concentration of P on the desorption of the sorbed Cu varied erratically with the concentration of added Cu. On average there was a decrease in the amount of desorbed Cu when the quantity of added DAP increased from 25 to 50 and 75 μmol P g soil^{-1}. The change in desorption of copper with increasing quantity of APP from 50 to 75 μmol P g soil^{-1} was negligible (Table 3.4).

The higher desorption of sorbed Cu in the presence of APP compared to DAP may be an indication of its low bonding energy on the polyphosphated surface. On the orthophosphated surface, Cu might have formed strong complexes with orthophosphate where Cu could act as a bridging cation between the two adjacently sorbed orthophosphate ions. A similar mechanism has been postulated for the sorption of Cd, Sr and Zn in the presence of orthophosphate by soil minerals (Helyar et al., 1976; Bolland et al., 1977). Since some of the polyphosphates solubilize and complex the native cations in their high affinity sites, the subsequently added Cu may gets sorbed to the then available low affinity sites. If so, Cu desorption in the presence of polyphosphate will be greater.

The difference between P pretreatments with respect to the desorption of Cu increased with concentration of added Cu (Fig. 3.4-3.6). The amount of desorbed Cu increased with the quantity of added Cu (Table 3.4). As the concentration of added Cu increased, more of the added Cu would go to sites with lower affinity and they will be easily desorbed. The relationship between the amount of Cu sorbed and the desorbed Cu is presented in Appendix 16.

Desorption of P was measured in the second and third equilibrations. Desorption of native P was low (Table 3.5). The portion of the sorbed P that was subsequently desorbed was higher for APP than DAP (contrasts). This might have resulted from the stronger bonding energy for orthophosphate sorption than for the polyphosphate sorption (Sutton and Larsen, 1964).

The amount of desorbed P tended to decrease with increasing concentration of added Cu particularly in second equilibration (Table 3.5). Phosphorus desorption increased linearly with added APP, and quadratically with added DAP at both equilibrations (orthogonal polynomials). Desorption of native P was greater in the third equilibration stage than in the second, while more of the added P was desorbed in the second step relative to the third. This low desorption of added P in the third step could result from the diffusion of added P to the interior of microaggregates with time.

The proportion of the sorbed P that was subsequently desorbed was less than the proportion of the desorbed Cu. It is hypothesized that the added orthophosphate and polyphosphate reacted with the unaltered soil mineral surfaces, and the native cations can act as the charge satisfying cations in the preferred sites by forming strong surface complexes. Consequently a major part of the added Cu might have been bonded to the low affinity sites (where complexed by unidentate mechanism as against bidentate) resulting in a greater desorption of the sorbed Cu compared to the desorption of sorbed P .

3.4 SUMMARY AND CONCLUSIONS

Pretreatment of soil with phosphate increased the subsequent sorption of Cu. The difference between APP and DAP, with respect to the sorbed Cu, increased with concentration of added P and Cu. Different types of Cu sorption isotherms were obtained depending on the P source and its concentrations. Partition coefficient of Cu sorption was higher when P was added as orthophosphate than as polyphosphate. Desorption of sorbed Cu was greater in the absence of added phosphates than in their presence. My results, which may simulate the Cu sorption reactions near a phosphate fertilizer granule in the field, indicate that application of polyphosphate form may increase the solution concentration of Cu more than orthophosphate does.

Table 3.1. Influence of the P pretreatments at different concentrations on the mean sorbed P and partition coefficient (Kd) of P

Treatments	Sorbed P (μmol P g soil^{-1})	Kd (mL g^{-1})
APP25	23.2(0.10)†	13.2(0.01)
APP50	46.2(0.10)	12.2(0.03)
APP75	68.9(0.11)	11.4(0.05)
DAP25	22.2(0.12)	8.15(0.04)
DAP50	44.1(0.01)	7.45(0.01)
DAP75	64.9(0.04)	6.43(0.05)

Orthogonal polynomials

	¶Sorbed P	§Kd
Linear	***	***
Quadratic	***	**

† standard error of mean (n=3); ANOVA for sorbed P and Kd for P sorption are given in Appendix 14; ¶ sorbed P = f (amount of P added); § Kd = f (amount of P added); ** significant at $P \geq 0.01$; *** significant at $P \geq 0.001$

Table 3.2 Influence of the P pretreatments on the amount of the subsequently sorbed Cu

Treatment	Amount of Cu addition (μmol Cu g soil^{-1})					
	3	6	9	12	15	Mean
	--------- Amount sorbed (μmol Cu g soil^{-1}) ----------------					
Control	2.87	5.73	8.49	11.1	14.0	8.43
	†(0.00)	(0.02)	(0.01)	(0.04)	(0.02)	
APP25	2.89	5.77	8.58	11.4	14.0	8.51
	(0.02)	(0.02)	(0.02)	(0.02)	(0.02)	
APP50	2.83	5.70	8.57	11.3	14.1	8.51
	(0.00)	(0.00)	(0.02)	(0.01)	(0.01)	
APP75	2.81	5.67	8.46	11.2	13.9	8.40
	(0.03)	(0.02)	(0.02)	(0.03)	(0.02)	
DAP25	2.94	5.87	8.79	11.7	14.3	8.74
	(0.02)	(0.00)	(0.04)	(0.01)	(0.03)	
DAP50	2.94	5.90	8.87	11.8	14.7	8.84
	(0.00)	(0.01)	(0.00)	(0.00)	(0.00)	
DAP75	2.87	5.84	8.78	11.7	14.7	8.79
	(0.02)	(0.00)	(0.00)	(0.02)	(0.00)	
L.S.D.(0.05)	0.057	0.042	0.072	0.071	0.058	

Contrasts	
Control vs Others	***
APP vs DAP	***
P at 25 vs P at 50	**
P at 25 vs P at 75	***
P at 50 vs P at 75	***
Control vs P at 25	**

¶Orthogonal Polynomials	Linear	Quadratic	Cubic
APP	**	**	NS
DAP	***	***	NS

---

† Standard error of mean (n = 3); ANOVA for sorbed Cu is given in Appendix 15; ¶ Cu sorbed = f (amount of P added); ** significant at P ≥ 0.01; *** significant at P ≥ 0.001; NS not significant

Table 3.3 Influence of the P pretreatments on the Kd of sorbed Cu at different concentrations of added Cu

Treatment	Amount of Cu addition (μmol Cu g soil^{-1}) 3	6	9	12	15	Mean
	Kd (mL g^{-1})					
Control	22.9 † (0.00)	21.5 (1.32)	16.6 (0.27)	11.8 (0.54)	13.9 (0.23)	17.3
APP25	26.8 (3.97)	25.6 (2.75)	20.7 (1.23)	17.6 (0.45)	13.3 (0.32)	20.8
APP50	16.3 (0.00)	19.1 (0.00)	19.9 (1.14)	16.9 (0.21)	16.2 (0.15)	17.7
APP75	15.3 (2.72)	17.2 (0.87)	15.6 (0.72)	13.1 (0.52)	12.8 (0.20)	14.8
DAP25	65.7 (2.85)	46.7 (0.00)	42.9 (8.12)	36.2 (0.91)	24.2 (1.32)	43.1
DAP50	46.6 (0.00)	58.0 (4.53)	70.5 (0.00)	57.7 (0.00)	52.0 (0.00)	57.0
DAP75	23.2 (3.02)	37.1 (0.00)	39.9 (0.00)	46.8 (2.99)	52.0 (0.00)	39.8
L.S.D.(0.05)	36.9	7.00	10.5	4.11	1.78	

Contrasts	
Control vs Others	***
APP vs DAP	***
P at 25 vs P at 50	*
P at 25 vs P at 75	***
P at 50 vs P at 75	***
Control vs P at 25	**

¶Orthogonal Polynomials

	Linear	Quadratic	Cubic
APP	**	NS	NS
DAP	***	***	NS

---

† Standard error of mean (n = 3); ANOVA in Appendix 15;

¶ Kd of Cu sorption = f (amount of P added); * significant at $P \geq 0.05$; ** significant at $P \geq 0.01$; *** significant at $P \geq 0.001$; NS not significant

Table 3.4 Influence of the P pretreatments on the desorption of Cu in the third equilibration

Treatment	Amount of Cu addition (μmol Cu g soil^{-1}) 0	3	6	9	12	15	Mean
	---------- Desorbed Cu (nmol Cu g soil^{-1}) ----------						
Control	0.16 †(0.00)	0.87 (0.08)	2.13 (0.08)	3.86 (0.08)	5.82 (0.00)	9.29 (0.00)	3.69
APP25	0.24 (0.08)	0.87 (0.08)	2.05 (0.00)	3.38 (0.08)	5.19 (0.16)	7.48 (0.08)	3.20
APP50	0.32 (0.00)	0.94 (0.00)	2.44 (0.08)	2.83 (0.00)	4.72 (0.16)	6.85 (0.08)	3.02
APP75	0.32 (0.16)	1.26 (0.00)	2.05 (0.00)	3.15 (0.16)	4.96 (0.08)	6.45 (0.16)	3.03
DAP25	0.47 (0.16)	1.02 (0.08)	1.57 (0.16)	2.60 (0.08)	3.70 (0.08)	5.59 (0.24)	2.49
DAP50	0.16 (0.00)	0.63 (0.00)	1.26 (0.16)	1.81 (0.08)	2.60 (0.08)	3.38 (0.08)	1.64
DAP75	0.32 (0.00)	0.87 (0.08)	1.26 (0.00)	1.73 (0.16)	2.13 (0.08)	2.68 (0.00)	1.50
L.S.D.(0.05)	0.30	0.20	0.31	0.34	0.34	0.40	

Contrasts	
Control vs Others	***
APP vs DAP	***
P at 25 vs P at 50	**
P at 25 vs P at 75	***
P at 50 vs P at 75	NS
Control vs P at 25	**

¶Orthogonal Polynomials	Linear	Quadratic	Cubic
APP	**	**	NS
DAP	***	***	NS

† Standard error of mean (n = 3); ANOVA in Appendix 15; ¶ desorbed Cu = f (amount of P added); * significant at $P \geq 0.05$; ** significant at $P \geq 0.01$; *** significant at $P \geq 0.001$; NS not significant

Table 3.5 Influence of the P pretreatments on the desorption of P in the second and third equilibrations at different amounts of added Cu

Treatments		Amount of Cu addition (μmol Cu g soil^{-1})					
	0	3	6	9	12	15	Mean
	Desorbed P (nmol P mL^{-1})						
Second equilibration							
Control	11.0	7.70	6.30	2.70	3.10	1.80	5.40
	(0.32)	(0.00)	(0.48)	(0.16)	(0.16)	(0.16)	
APP25	492	468	446	436	417	400	443
	(2.42)	(1.13)	(1.29)	(12.3)	(1.45)	(1.29)	
APP50	975	921	889	883	826	798	882
	(25.1)	(30.9)	(9.04)	(15.2)	(14.0)	(3.07)	
APP75	1397	1423	1369	1294	1211	1182	1313
	(3.55)	(8.39)	(1.45)	(0.32)	(1.94)	(13.1)	
DAP25	281	267	262	257	264	254	264
	(0.97)	(4.04)	(2.26)	(1.61)	(2.26)	(4.36)	
DAP50	477	482	504	470	487	462	480
	(10.5)	(0.00)	(3.55)	(12.9)	(10.7)	(0.65)	
DAP75	667	673	671	658	632	651	659
	(11.1)	(29.1)	(9.20)	(24.2)	(17.6)	(3.39)	
L.S.D	37.7	55.0	17.3	42.6	31.8	18.4	

Contrasts	
Control vs Others	***
APP vs DAP	***
P at 25 vs P at 50	**
P at 25 vs P at 75	***
P at 50 vs P at 75	*
Control vs P at 25	**

¶Orthogonal Polynomials	Linear	Quadratic	Cubic
APP	**	NS	NS
DAP	***	***	NS

---

† Standard error of mean (n = 3); ANOVA in Appendix 17; ¶ desorbed P = f (amount of P added); * significant at $P \geq 0.05$; ** significant at $P \geq 0.01$; *** significant at $P \geq 0.001$; NS not significant

Table 3.5 (Contd.)

Treatments	Amount of Cu addition (μmol Cu g soil^{-1})						
	0	3	6	9	12	15	Mean
	Desorbed P (nmol P mL^{-1})						
Third equilibration							
Control	28.9 †(0.65)	24.2 (1.61)	26.2 (0.32)	25.8 (1.61)	21.8 (0.16)	26.2 (0.32)	24.8
APP25	267 (8.23)	261 (2.10)	267 (0.32)	257 (3.23)	257 (1.29)	264 (4.20)	262
APP50	434 (1.45)	417 (0.32)	428 (0.32)	403 (4.68)	420 (0.81)	413 (11.1)	419
APP75	512 (2.09)	556 (2.9)	534 (2.58)	495 (7.91)	495 (15.2)	496 (5.0)	496
DAP25	141 (1.61)	131 (0.32)	140 (0.16)	148 (0.48)	129 (3.71)	123 (10.65)	135
DAP50	190 (0.7)	186 (5.33)	180 (13.2)	182 (3.55)	175 (1.78)	176 (0.65)	181
DAP75	241 (0.16)	245 (5.33)	244 (7.26)	228 (3.07)	236 (5.17)	235 (0.16)	238
L.S.D.	22.1	19.2	19.4	13.8	21.0	19.7	

Contrasts	
Control vs Others	***
APP vs DAP	***
P at 25 vs P at 50	**
P at 25 vs P at 75	***
P at 50 vs P at 75	*
Control vs P at 25	**

¶Orthogonal Polynomials	Linear	Quadratic	Cubic
APP	**	NS	NS
DAP	***	***	NS

---

† Standard error of mean (n = 3); ANOVA table in Appendix 17; ¶ desorbed P = f (amount of P added); * significant at $P \geq 0.05$; ** significant at $P \geq 0.01$; *** significant at $P \geq 0.001$; NS not significant

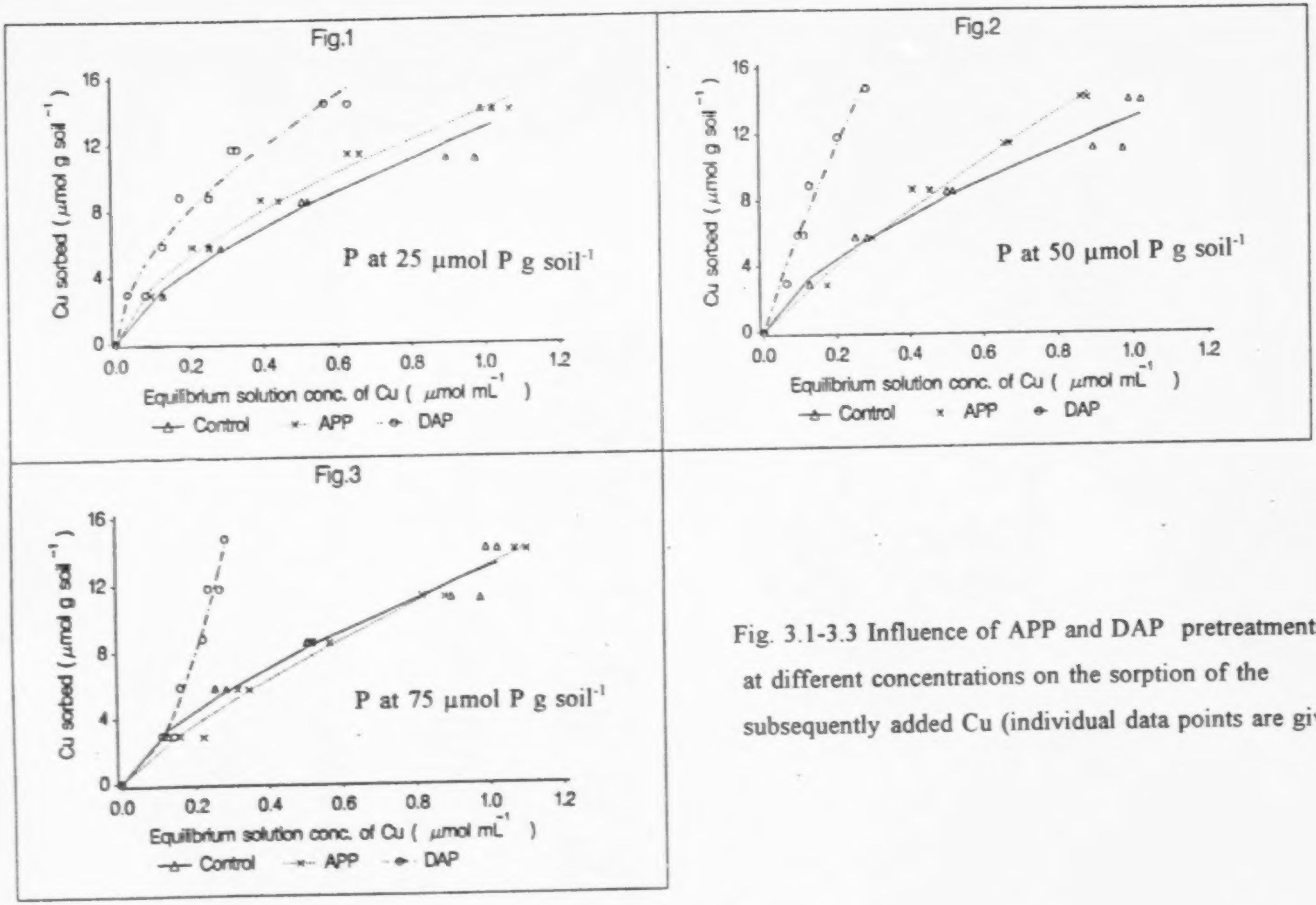


Fig. 3.1-3.3 Influence of APP and DAP pretreatments at different concentrations on the sorption of the subsequently added Cu (individual data points are given)

Fig.4

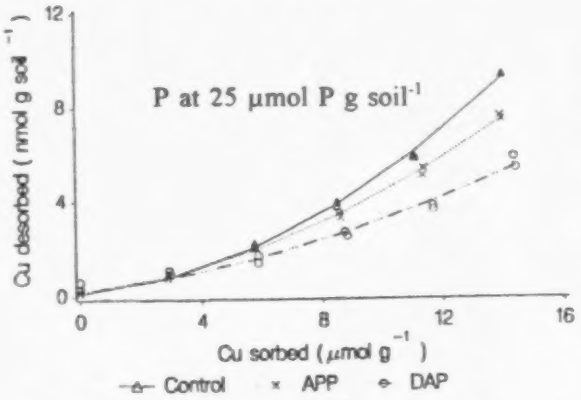


Fig.5

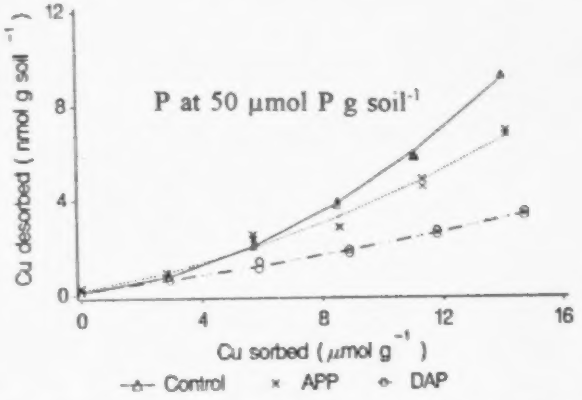


Fig.6

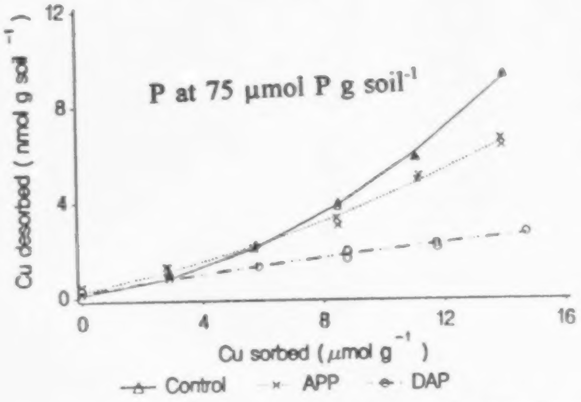


Fig. 3.4-3.6 Influence of APP and DAP pretreatments at different concentrations on the desorption of the sorbed Cu (individual data points are given)

3.5 REFERENCES

Al-Kanani, T., and A.F. MacKenzie. 1991. Sorption and desorption of orthophosphate and pyrophosphate by mineral fractions of soils, goethite and kaolinite. Can. J. Soil Sci. 71: 327-338.

Asher, L.E., and B. Bar-Yosef. 1982. Pyrophosphate, EDTA and DTPA dependent Zn adsorption by montmorillonite. Soil Sci. Soc. Am. J. 46: 271-276.

Bar-Yosef, B., and L.E. Asher. 1983. Reactions of pyrophosphate in soils and its effect on Zn sorption at various pH levels. Soil Sci. 136: 82-88.

Blanchar, R.W., and L.R. Hossner. 1969a. Hydrolysis and sorption of ortho-, pyro, tripoly- and trimetaphosphate in 32 midwestern soils. Soil Sci. Soc. Am. Proc. 33: 622-625.

Blanchar, R. W., and L. R. Hossner. 1969b. Hydrolysis and sorption reactions of orthophosphate, pyrophosphate and tripolyphosphate anions added to an Elliot Soil. Soil Sci. Soc. Am. Proc. 33: 141-144.

Bolland, M. D. A., A. M. Posner, and J. P. Quirk. 1977. Zn adsorption by goethite in the absence and presence of phosphate. Aust. J. Soil Res. 15: 279-286.

Boyd, S. A., L. E. Sommers, D.W. Nelson, and D.K. West. 1981. The mechanism of Cu (II) binding by humic acid: An electron spin resonance study of a Cu (II)-humic acid complex and some adducts with N donors. Soil Sci. Soc. Am. J. 45: 745-749.

Corbridge, D.E.C. 1985. Phosphorus: An outline of its chemistry, biochemistry and technology. 3rd ed. Elsevier Sci. Publ., New York.

Davis, J. A., and J.O. Leckie. 1978. Effect of adsorbed complexing ligands on trace metal uptake by hydrous oxides. Environ. Sci. Technol. 12: 1309-1325.

Dick, R.P., and M.A. Tabatabai. 1986. Hydrolysis of polyphosphates in soils. Soil Sci. 142: 132-140.

Elliot, H. A., and C. P. Huang. 1980. Adsorption of some Cu (II)- amino acid complexes at the solid-solution interface. Effect of ligand and surface hydrophobicity. Environ. Sci. Technol. 14: 87-93.

Elliot, H. A., and C. P. Huang. 1981. Adsorption characteristics of some Cu (II) complexes on aluminosilicates. Water Res. 15: 849-855.

Eze, O.C., and P. Loganathan. 1990. Effects of pH on phosphate sorption of some paleudults of southern Nigeria. Soil Sci. 150: 613-621.

Gillman, G.P., and R.L. Fox. 1980. Increases in the cation exchange capacity of variable charge soils following superphosphate applications. Soil Sci. Soc. Am. J. 44: 934-938.

Giordano, P.M., E.C. Sample, and J.J. Mortvedt. 1971. Effect of ammonium ortho- and pyrophosphate on Zn and P in soil solution. Soil Sci. 111: 101-106.

Gregor, J.E. and H.K.J. Powell. 1986. Acid pyrophosphate extraction of soil fulvic acids. J. Soil Sci. 37: 577-585.

Harter, R. D. 1983. Effect of soil pH on adsorption of Pb, Cu, Zn and Ni. Soil Sci. Soc. Am. J. 47: 47-51.

Hashimoto, I., J.D. Hughes, and O.D. Philen. 1969. Reactions of triammonium pyrophosphate with soils and soil minerals. Soil Sci. Soc. Am. Proc. 33: 401-405.

Hayes, K. F., and J.O. Leckie. 1986. Mechanism of lead ion adsorption at goethite-water interface. p. 114-141. *In* J.A. Davis, and K.F. Hayes (ed.) Geochemical processes at mineral surfaces. Am. Chem. Soc. Symposium Series. No. 323. Am. Chem. Soc. Washington.

Helyar, K. R., D. N. Munns, and R. G. Burau. 1976. Adsorption of phosphate by gibbsite II. Formation of a surface complex involving divalent cations. J. Soil Sci. 27: 315-323

Kuo, S., and B. L. McNeal. 1984. Effects of pH and phosphate on Cd sorption by hydrous ferric oxide. Soil Sci. Soc. Am. J. 48: 1040-1044.

Lemare, P.H., and L.A. Leon. 1989. The effects of lime on adsorption and desorption of phosphate in five Colombian soils. J. Soil Sci. 40: 59-69.

Lindsay, W. L., A.W. Frazier, and H.F. Stephenson. 1962. Identification of reaction products from P fertilizers in soil. Soil Sci. Soc. Am. Proc. 26: 446-452.

McBride, M.B. 1978. Transition metal bonding in humic acid. Soil Sci. 126: 200-209.

McBride, M. B., A.R. Fraser, and W.J. McHardy. 1984. Cu^{2+} interaction with microcrystalline gibbsite. Evidence for oriented chemisorbed Cu ions. Clays Clay Miner. 32: 12-18.

McBride, M.B. 1985a. Sorption of Cu (II) on aluminum hydroxide as affected by phosphate. Soil Sci Soc. Am. J. 49: 843-846.

McBride, M.B. 1985b. Influence of glycine on Cu^{2+} adsorption by microcrystalline gibbsite and boehemite. Clays Clay Miner. 33: 397-402.

McLaren, R.G., and D.V. Crawford. 1973. Studies on soil Cu. II. The specific adsorption of Cu by soils. J. Soil Sci. 24: 444-452.

McLaren, R.G., R.S. Swift and J. G. Williams. 1981. The adsorption of Cu by soil materials at low equilibrium solution concentrations. J. Soil Sci. 32: 247-256.

McLaren, R.G., J. G. Williams, and R.S. Swift. 1983. Some observations on the desorption and distribution behaviour of Cu with soil components. J. Soil Sci. 34: 325-331.

Mnkeni, P.N.S. and A.F. MacKenzie. 1985. Retention of ortho- and polyphosphates in some Quebec soils as affected by added organic residues and calcium carbonate. Can. J. Soil. Sci. 65: 575-585.

Mortvedt, J.J., and G. Osborn. 1977. Micronutrient concentrations in soil solution after ammonium phosphate applications. Soil Sci. Soc. Am. J. 41: 1004-1009.

Msaky, J.J., and R. Calvet. 1990. Adsorption behaviour of Cu and Zn in soils: Influence of pH on adsorption characteristics. Soil Sci. 150: 513-523.

Neilsen, D., P.B. Hoyt, and A.F. MacKenzie. 1986. Distribution of soil Zn fractions in British Columbia interior orchard soils. Can. J. Soil Sci. 66: 445-454.

SAS Institute Inc. 1987. SAS/STAT guide for personal computers. Version 6 Edition, Cary, N. C: SAS Institute Inc.

Sayin, M., A.R. Mermut, and H. Tissen. 1990. Phosphate sorption-desorption characteristics by magnetically separated soil fractions. Soil Sci. Soc. Am. J. 54: 1298-1304.

Sibanda, H.M., and S.D. Young. 1986. Competitive adsorption of humus acids and phosphate on goethite, gibbsite and two tropical soils. J. Soil Sci. 37:

197-204.

Sutton, C.D., and S. Larsen. 1964. Pyrophosphate as a source of phosphorus for plants. Soil Sci. 97: 196-201.

Xie, R.J., and A.F. MacKenzie. 1989. Effects of sorbed orthophosphate on Zn status in three soils of eastern Canada. J. Soil Sci. 40: 49-58.

Xie, R.J., and A.F. MacKenzie. 1990. Sorbed ortho- and pyrophosphate effects on Zn reactions compared in three autoclaved soils. Soil Sci. Soc. Am. J. 54: 744-750.

Chapter 4

SORPTION OF Cu AT LOW CONCENTRATION: INFLUENCE OF POLYPHOSPHATE AND ORTHOPHOSPHATE

4.1 INTRODUCTION

Sorption mechanisms and rates are dependent on time of reaction and the concentration of added solutes (Rajan and Fox, 1972; Barrow and Shaw, 1975; Holford and Mattingly, 1975; Bruemmer et al., 1988). Soils contain a variety of organic and inorganic components each having a continuum of complexing sites with different affinities for metals (McBride 1982; Clark and McBride 1984). Phosphate reactions in soils influence trace element chemistry by changing the surface characteristics of the adsorbing components and the soil solution properties (Elkhatib and Hern, 1988; Naidu et al., 1990; Pardo and Guadalix, 1990; Barrow, 1991). Bolan et al., (1985) suggested that an increase in phosphate sorption with time by iron and aluminium hydroxides is caused by a redistribution of adsorbed phosphates to the interior of the adsorbing particles by solid state diffusion. The driving force for the diffusive process in this redistribution process, is the surface concentration of the adsorbate and not the solution concentration. This may cause a change in the sorption of Cu with time in a P treated soil.

Reactions of orthophosphate will change with time depending on the added concentration (Pierzynski et al., 1990). Concentrated P solutions dissolve soil minerals (Kittrick and Jackson, 1956; Veith and Sposito, 1977; Karathanasis et al., 1983) and make a number of elements available for precipitation that were not present in the P carrier. Therefore in the time between a P fertilizer application and its dilution with soil pore water a variety of P-rich precipitates is possible. However reactions of P with soil solids are different at low added concentration.

Desorption of the sorbed ions is also dependent on the extent of metal loading. At low loading, metals will occupy only the most specific sorption sites by forming covalent bonds, and therefore will be incompletely desorbed. As the metal loading increases, sorption on sites with lower affinity will also occur (Boyd et al., 1981) and the desorption will be relatively high.

Chemical reactions of orthophosphates (the form of P in the conventional fertilizers) and polyphosphates are different in soil. Polyphosphates are vulnerable to biological hydrolysis (Subbarao et al.,1977; Dick and Tabatabai, 1987) resulting in different chain lengths with time, and their chemical behaviour depends on the chain length. This may cause a change in the sorption behaviour of added metals including Cu. However, information on the sorption reactions of Cu at low concentrations after the pretreatment of soil with polyphosphate is lacking. In addition, most of the sorption-desorption experiments have been conducted at high concentrations and for relatively short periods even though the slow and continuing process that follows adsorption is important in the long term reactions of solutes with soil. The sorption and desorption of P and Cu when added at low concentration over different times is pertinent, because Cu and P fertilizers become diluted in the soil solution with time and crop removal continues to withdraw the two nutrients. Therefore the objective of this incubation experiment was to determine the effect of time of reaction of APP and DAP with soil on the subsequent sorption of Cu at low concentration.

4.2 MATERIALS AND METHODS

A Cu deficient soil sample studied in earlier experiments (Chapter 2 and 3) was used. It was air-dried and passed through <1 mm sieve. Some characteristics of the soil are given in Table 2.1. Before running the Cu sorption isotherms, soils were pretreated with ammonium polyphosphate (APP) and diammonium phosphate (DAP) at two concentrations, and incubated for different time periods (20, 40, 60 and 80 days). Ammonium polyphosphate and DAP at 15 and 30 μg P g soil^{-1} were dissolved in water, mixed with soil (300 g), and placed in plastic containers with perforations in the lids. The control treatment received only distilled, deionized water. Containers were placed in a completely randomized design in an incubator at 25°C. All treatments were replicated three times. Soil moisture content was maintained at 60 per cent of the moisture held at field capacity using deionized distilled water.

Pretreated soil samples were withdrawn at 20 day intervals for 80 days to determine the Cu sorption isotherms using 3 g soil and 30 mL solution. Solutions were prepared in 0.03M $KClO_4$ and the concentrations of Cu used were 0, 2, 4, 6, 8, 10 µg Cu g soil^{-1} (i.e. 0, 0.03, 0.06, 0.09, 0.13, 0.16 µmol Cu g soil^{-1}). Treatments at each concentration of Cu at each time were: Control, APP15, APP30, DAP15 and DAP30. Thus there were 90 experimental units at each time of sampling. The greatest concentration of Cu used was only 10 µg Cu g soil^{-1} because in a previous experiment (Chapter 2) that application was sufficient to correct the Cu deficiency symptoms of wheat. After the addition of the solutions to 3-g soil samples, the pH of the suspensions was adjusted to 5.80 ± 0.02, and the mixtures were equilibrated for 48 hours on a reciprocating shaker. They were then centrifuged for 20 minutes at 22000 RPM and the solution concentrations of total P and Cu (ionic and complexed) were determined in the supernatant solution by Inductively Coupled Plasma Emission Spectroscopy. The amount of sorbed Cu was calculated from the initial and the final equilibrium solution concentrations of Cu. The Freundlich adsorption isotherm equation was used (because of higher R^2 than for the Langmuir equation) to determine the relation of the sorbed Cu and the equilibrium concentration of Cu.

$q=K\,C^{(1/n)}$ where

q is the amount of Cu sorbed (µg Cu g soil^{-1})

C is the equilibrium concentration of Cu (µg Cu mL^{-1})

K and n are constants

The parameters, along with the standard error of estimates in the Freundlich equation, are given in Table 4.6. The partition coefficient (Kd) was calculated as the ratio of the amount of the sorbed Cu to the final equilibrium solution concentration at a particular level of addition.

Statistical analysis

Analysis of variance at each concentration of Cu and each time (15 experimental units), and over all Cu concentrations at each time (90 experimental units) for Cu sorption, Kd of Cu sorption and P desorption were done using PROC GLM in SAS (SAS Institute, 1987). Homogeneity of error variance was tested by plotting the residuals against the predicted values using PROC PLOT, and the normality of error was tested using PROC UNIVARIATE. Contrasts were used for comparing the P sources and rates. Orthogonal polynomials were used to find the effect of P application rates on the sorbed Cu, Kd, and desorbed P. Comparisons of individual P pretreatments at each Cu concentration at each sampling time were made using LSD. Parameters of the Freundlich adsorption isotherm equation were calculated with PROC NLIN (Appendix 20), and PROC GPLOT was used for generating the graphs.

4.3 RESULTS AND DISCUSSION

4.3.1 SORPTION OF Cu

Forms of added P and the time after the P pretreatment influenced the sorption of the subsequently added Cu (Table 4.1). The mean amount of Cu sorbed (average of all concentrations of Cu) tended to decrease up to 60 days of P pretreatment, except for APP30, but increased when the pretreatment duration was 80 days.

When the quantity of added APP increased, the mean sorbed Cu was less (5.88 μg Cu g soil^{-1} for APP15 and 5.86 for APP30) at 20 days, and more (5.87 μg Cu g soil^{-1} for APP15 and 5.88 for APP30) at 40 days (Table 4.1 and 4.2; orthogonal polynomials). By contrast, Cu sorption increased with the quantity of added DAP at all sampling times (Table 4.1 and 4.2; orthogonal polynomials). The difference in Cu sorption following APP and DAP pretreatments was greater when the P sources were added at 30 compared to 15 μg P g soil^{-1} (Fig. 4.1-4.8).

Most of the added Cu was sorbed in all the P treated soils. For a given amount of added Cu, the equilibrium solution concentration of Cu was maximum when there was no added P (Fig.4.1-4.8). Between the P sources, APP pretreatment had higher solution concentration of Cu than DAP pretreatment at a given amount of added Cu. For example, at 20 days after P pretreatment, the solution Cu concentrations in the control, APP30 and

DAP30 treatments, were 0.11, 0.09 and 0.06 μg Cu mL^{-1} respectively, at an added Cu concentration of 6 μg Cu g $soil^{-1}$ (Table 4.1).

Pretreatment (P) x Concentration (Cu concentration) interaction was significant only at 20 days after P pretreatment (Appendix 18). Regardless of the pretreatment duration, orthophosphate added at 30 μg P g $soil^{-1}$ resulted in the greatest Cu sorption at all concentrations of Cu (Fig. 4.1 - 4.4).

The partition coefficient (Kd) of Cu was influenced by the form of the added P (Table 4.3). At all four sampling times, the effect of Cu concentration and the P pretreatments on Kd were significant, but the P Pretreatment x Concentration (Cu) interaction was not significant (Appendix 19). Hence, the mean Kd (average of all added concentrations of Cu) at each time was taken for comparison of P treatment means. Mean Kd for Cu sorption was higher when the soil was pretreated with DAP than with APP (Table 4.3, contrasts). This indicated that APP had reduced the sorption of Cu compared to DAP. Partitioning of Cu was similar in the control and in APP pretreatments. The mean partition coefficient of Cu (average of concentration) tended to decrease with time up to 60 days of pretreatment with DAP at both levels, and APP at 30 μg P g $soil^{-1}$. In the control and when APP was added at 15 μg P g $soil^{-1}$ the Kd decreased only until 40 days after pretreatment. The Kd was greatest when DAP was added at 30 μg Cu g $soil^{-1}$. The Kd of Cu sorption increased quadratically with amounts of DAP except at 80 days (orthogonal polynomials).

The Cu sorption isotherm was a C-curve (constant partition) for all treatments except the control at 20 days after P pretreatment, and when DAP was added at 30 μg P g $soil^{-1}$ at 60 days of pretreatment (Fig. 4.1- 4.8).

There are several possible explanations for the different amount of sorbed Cu after pretreatment with APP and DAP. Probable chemisorption sites for the sorption of Cu are the broken edges of clay minerals, and the sites on the amorphous Fe and Al oxides. Most of the added P would have been sorbed to the high bonding energy sites (where it can form a bidentate linkage) because the added concentration of P was low. Difference in sorption of Cu between APP and DAP was probably the result of their different orientation on the sorption surfaces. Orientation of the single tetrahedron of orthophosphates on the adsorbing components might have provided a more favourable site for Cu sorption than could occur with polyphosphate. However, the possibility of getting enough adjacent sites for orthophosphate sorption where Cu could act as a bridging cation may be low at low added DAP concentration. Consequently the possible mechanisms of Cu sorption at low concentration of added DAP are: 1) direct sorption to the unaltered high-affinity sites on the mineral surface (Fe-O-, Al-O-), 2) formation of ternary complexes with orthophosphate and the mineral surface (Clark and McBride, 1985; McBride, 1985a), and 3) bonding to the divalent adsorbed orthophosphate by a unidentate mechanism. A previous experiment also showed lower sorption of Cu in the presence of polyphosphate as compared to orthophosphate even when the concentrations of added P and Cu were higher than in this experiment (Chapter 3).

Explanations for the low sorption of Cu after APP pretreatment are as follows. First, the nonhydrolyzed APP is in a polymerized form and it may reduce the sorption of Cu by physically blocking the existing adsorption sites. Secondly, APP may solubilize soil organic matter leading to the formation of soluble Cu-organic complexes. Thirdly, APP before hydrolysis may form direct soluble Cu-complexes (Cu-polyphosphate complexes). However, the formation of soluble complexes depends on the metal/ligand ratio. Under high ligand concentrations the formation of soluble complexes is high (McBride, 1985b). Therefore a decrease in the sorption of added Cu with increase in added APP at 20 days after P pretreatment may be an indication of the direct soluble complex formation of added Cu (Cu-polyphosphate complexes) at high concentration of APP. When polyphosphates are added at low concentration, the direct complex formation with cation is low (Asher and Bar-Yosef, 1982) and the biological hydrolysis may be high. Consequently, the sorption of Cu may be higher in APP30 than in APP15 treatments. Hydrolysis of polyphosphates with time might have resulted in less soluble APP-Cu complex formation leading to increased Cu sorption with time of incubation.

Barrow (1983) suggested that an initial fast sorption reaction followed by a slow process of particle diffusion into the interior of the peds accompanied P addition. The diffusion of P into peds could have led to a decline in the number of surface negative sites and that process might have resulted in decreasing Cu sorption with time up to 60 days after P pretreatment. In addition, when P was added to the soil, some of the native cations, depending on their ionic size, would act as the bridging cations for the adsorbed P (Helyar et al., 1976). Hence with time, regardless of the P sources the sites available for Cu sorption will become fewer, resulting in its low sorption.

Increase in the sorption of added Cu with greater addition of orthophosphate implies greater occupation of orthophosphate on adjacent sites where Cu can be the bridging cation. At low site coverage by P, the distance between the occupied sites would result in a reduced surface complex formation of orthophosphate and cations (Helyar et al., 1976).

4.3.2 DESORPTION OF P

Desorption of P was influenced by the P pretreatment and concentrations of added Cu (Table 4.4; Appendix 21). Desorbed P was greater when the pretreatment was with APP than with DAP (Table 4.4 and 4.5, contrasts). Desorbed P decreased with time of incubation and increased with the quantity of added P, except for DAP at 20 days (Table 4.4 and 4.5). Desorption of P was higher with APP than with DAP, both applied at 30 μg P g soil^{-1} at 40 and 60 days after pretreatment. There were 18 and 72 per cent more desorption of P over the control in APP pretreatments than in DAP pretreatments at 15 and 30 μg P g soil^{-1} respectively. The desorbed P from the control treatment represented the desorption of native P.

The decrease of desorbed P with greater P pretreatment time might indicate the diffusion of P into the soil peds and/or the transformation of new P-enriched particles into a more crystalline form with high bonding energy. Phosphate sorbed with low bonding energy or low adsorption energy will be desorbed more easily compared to the one with high bonding energy. The higher desorption of P from APP than DAP pretreatments, when both added at 30 μg P g soil^{-1} might be the result of the low sorption energy for the polyphosphate and its ability to solubilize soil organic matter. Some of the organic anions produced during the solubilization of organic matter may compete for the adsorbing sites leading to the sorption of P on remaining sites with low bonding energy resulting in subsequent high desorption (Holford and Mattingly, 1975; Sibanda and Young, 1986; Kafkafi et al., 1988). As the concentration of added P increases, a larger portion of P might be held by sites with low affinities (Syers et al., 1973; Holford et al., 1974) and desorption from these low affinity sites will be easier compared to those on high affinity sites, and therefore desorption increased as the quantity of added P increased.

4.4 SUMMARY AND CONCLUSIONS

Sources of P when added at 30 μg P g soil^{-1}, and the duration of P pretreatment influenced the sorption of the subsequently added Cu. Pretreatment with DAP resulted in greater sorption of Cu than occurred with control or APP. The Kd of Cu was low in the control and following pretreatment with APP, but it increased with concentrations of added P. Desorption of sorbed P after APP pretreatment was greater than that after DAP pretreatment. Lower sorption of Cu after pretreatment with APP than with DAP is consistent with greater plant uptake of Cu from APP treatments than from DAP treatments in the earlier greenhouse experiment (Chapter 2).

Table 4.1 The amount of sorbed Cu with different Cu additions at 20,40, 60 and 80 days after the P pretreatment

Treatments	Amount of Cu addition (µg Cu g soil^{-1})					
	2	4	6	8	10	Mean
	Sorbed Cu (µg Cu g soil^{-1})					
20 days						
Control	1.92(0.000)†	3.89(0.006)	5.89(0.003)	7.83(0.003)	9.82(0.003)	5.87
APP15	1.94(0.003)	3.91(0.003)	5.91(0.007)	7.85(0.003)	9.81(0.003)	5.88
APP30	1.94(0.006)	3.90(0.003)	5.91(0.003)	7.84(0.007)	9.83(0.003)	5.86
DAP15	1.94(0.000)	3.92(0.003)	5.93(0.003)	7.86(0.006)	9.87(0.003)	5.90
DAP30	1.96(0.003)	3.93(0.003)	5.94(0.000)	7.88(0.013)	9.87(0.000)	5.92
L.S.D.(0.05)	0.011	0.012	0.012	0.024	0.023	
40 days						
Control	1.92(0.003)	3.89(0.003)	5.91(0.003)	7.82(0.006)	9.80(0.010)	5.87
APP15	1.92(0.003)	3.89(0.003)	5.92(0.003)	7.81(0.003)	9.80(0.020)	5.87
APP30	1.93(0.003)	3.89(0.006)	5.91(0.003)	7.84(0.012)	9.81(0.012)	5.88
DAP15	1.93(0.003)	3.90(0.003)	5.92(0.006)	7.84(0.009)	9.82(0.012)	5.88
DAP30	1.95(0.003)	3.92(0.003)	5.94(0.000)	7.89(0.007)	9.86(0.003)	5.91
L.S.D.(0.05)	0.011	0.012	0.012	0.025	0.040	

† Standard error of mean (n=3); ANOVA for the sorption of Cu at 20, 40, 60 and 80 days are given in Appendix 18

Table 4.1 (Contd.)

Treatments	Amount of Cu addition (μg Cu g soil^{-1})					
	2	4	6	8	10	Mean
	Sorbed Cu (μg Cu g soil^{-1})					
60 days						
Control	1.91(0.003)†	3.87(0.003)	5.90(0.003)	7.86(0.062)	9.77(0.009)	5.86
APP15	1.92(0.003)	3.87(0.003)	5.90(0.000)	7.79(0.006)	9.76(0.009)	5.85
APP30	1.91(0.006)	3.86(0.003)	5.90(0.006)	7.80(0.009)	9.77(0.003)	5.85
DAP15	1.91(0.000)	3.87(0.003)	5.90(0.003)	7.81(0.000)	9.77(0.003)	5.85
DAP30	1.93(0.003)	3.90(0.000)	5.92(0.003)	7.86(0.003)	9.84(0.006)	5.89
L.S.D.(0.05)	0.012	0.009	0.012	N.S.	0.021	
80days						
Control	1.96(0.000)	3.93(0.003)	5.94(0.003)	7.88(0.006)	9.86(0.003)	5.92
APP15	1.96(0.003)	3.93(0.003)	5.94(0.003)	7.88(0.003)	9.87(0.014)	5.91
APP30	1.96(0.003)	3.93(0.003)	5.94(0.003)	7.88(0.010)	9.86(0.009)	5.92
DAP15	1.96(0.003)	3.93(0.003)	5.94(0.006)	7.88(0.000)	9.86(0.003)	5.91
DAP30	1.96(0.000)	3.93(0.003)	5.95(0.000)	7.90(0.003)	9.88(0.003)	5.93
L.S.D.(0.05)	N.S.	N.S.	N.S.	0.018	N.S.	

† Standard error of mean (n=3);

Table 4.2 Contrasts and orthogonal polynomials showing the effect of different amounts of P pretreatments on the sorption of Cu

Contrasts	20 days	40 days	60 days	80 days
Control vs Others	***	***	NS	NS
APP vs DAP	**	***	***	**
P at 15 vs P at 30	***	**	**	**
P at 15 vs Control	***	***	***	**

¶Orthogonal polynomials	20 days		40 days		60 days		80 days	
	L‡	Q§	L	Q	L	Q	L	Q
APP	***	NS	*	NS	NS	NS	NS	NS
DAP	***	NS	***	*	**	**	**	**

---

* significant at P ≥ 0.05; ** significant at P ≥ 0.01; *** significant at P ≥ 0.001; NS not significant;

¶ Cu sorbed = f (amount of added P); ‡ Linear response; § Quadratic response

Table 4.3. Influence of time and P pretreatments on the partition coefficient (Kd) of Cu (over all concentrations of Cu)

Treatment	Days after the pretreatment of P 20 days	40 days	60 days	80 days	Mean
	Kd				
Control	74.2	52.6	54.9	79.0	65.2
APP15	72.3	52.5	53.5	76.0	63.6
APP30	71.8	56.2	51.1	85.1	66.0
DAP15	78.8	59.0	57.4	82.5	69.4
DAP30	99.4	89.0	84.2	109	95.2
L.S.D.(0.05)	6.8	5.7	5.1	9.7	3.60

Contrasts	20 days	40 days	60 days	80 days
Control vs Others	**	***	**	**
APP vs DAP	***	***	***	***
P at 15 vs P at 30	***	**	***	***
P at 15 vs Control	***	*	***	***

¶Orthogonal polynomials	20 days		40 days		60 days		80 days	
	L‡	Q§	L	Q	L	Q	L	Q
APP	NS	NS	NS	NS	NS	NS	NS	NS
DAP	***	***	***	**	***	***	*	NS

---

* significant at $P \geq 0.05$; ** significant at $P \geq 0.01$; *** significant at $P \geq 0.001$; NS not significant; ¶ Kd = f (amount of added P); ‡ Linear response; § Quadratic response; ANOVA for Kd at 20, 40, 60, and 80 days are given in Appendix 19

Table 4.4 Desorption of P with different amount of Cu additions at 40, 60 and 80 days after the P pretreatments

	Amount of Cu addition (μg Cu g soil^{-1})						
Treatments	0	2	4	6	8	10	Mean
	Desorbed P (μg P mL^{-1})						
40 days							
Control	1.76(0.25)†	1.86(0.06)	1.93(0.13)	1.94(0.08)	1.84(0.04)	1.75 (0.10)	1.85
APP15	2.49(0.17)	2.47(0.08)	2.33(0.08)	2.17(0.08)	2.30(0.03)	2.22 (0.18)	2.33
APP30	2.74(0.07)	2.78(0.09)	2.84(0.12)	2.91(0.16)	2.46(0.16)	2.47 (0.08)	2.70
DAP15	2.32(0.07)	2.51(0.41)	2.12(0.03)	2.16(0.08)	2.02(0.06)	1.90 (0.10)	2.17
DAP30	2.00(0.04)	2.01(0.04)	2.17(0.05)	2.10(0.04)	1.95(0.08)	1.98 (0.01)	2.04
L.S.D.(0.05)	0.45	0.61	0.28	0.30	0.27	0.36	0.09
60 days							
Control	1.09(0.03)	1.18(0.09)	1.14(0.09)	1.15(0.07)	1.07(0.03)	1.18(0.05)	1.14
APP15	1.46(0.04)	1.51(0.07)	1.48(0.04)	1.52(0.03)	1.39(0.19)	1.48(0.07)	1.47
APP30	1.61(0.11)	1.88(0.12)	1.76(0.11)	1.81(0.07)	1.79(0.04)	1.80(0.04)	1.77
DAP15	1.38(0.07)	1.51(0.06)	1.57(0.05)	1.56(0.13)	1.57(0.02)	1.57(0.04)	1.53
DAP30	1.24(0.02)	1.44(0.10)	1.72(0.04)	1.59(0.09)	1.58(0.08)	1.70(0.04)	1.55
L.S.D.(0.05)	0.18	0.29	0.22	0.27	0.29	0.15	0.15

† Standard error of mean (n=3); ANOVA for the desorption of P at 40, 60 and 80days are given in Appendix 21

Table 4.4 (Contd.)

Treatments	Amount of Cu addition (μg Cu g soil^{-1}) 0	 2	 4	 6	 8	 10	Mean
	Desorbed P (μg P mL^{-1})						
80 days							
Control	0.75(0.02)†	0.73(0.03)	0.72(0.02)	0.74(0.01)	0.77(0.01)	0.81(0.01)	0.75
APP15	1.12(0.01)	1.09(0.02)	1.10(0.02)	1.11(0.05)	1.08(0.01)	1.12(0.05)	1.10
APP30	1.43(0.01)	1.41(0.02)	1.43(0.04)	1.33(0.03)	1.40(0.03)	1.40(0.01)	1.40
DAP15	1.10(0.03)	1.05(0.01)	1.04(0.01)	0.98(0.02)	1.00(0.02)	1.02(0.01)	1.03
DAP30	1.39(0.02)	1.39(0.06)	1.42(0.03)	1.39(0.06)	1.38(0.08)	1.39(0.03)	1.39
L.S.D(0.05)	0.62	0.95	0.80	0.11	0.12	0.09	0.04

† Standard error of mean (n=3)

Table 4.5 Contrasts and orthogonal polynomials showing the response of the mean amount of P desorption to different amounts of application of APP and DAP

Contrasts	40 days	60 days	80 days
Control vs Others	***	***	***
APP vs DAP	**	**	***
P at 15 vs P at 30	***	***	**
P at 15 vs Control	***	NS	***

¶Orthogonal polynomials	40 days		60 days		80 days	
	L‡	Q§	L	Q	L	Q
APP	***	NS	***	NS	***	NS
DAP	***	***	***	**	*	**

---

* significant at P ≥ 0.05; ** significant at P ≥ 0.01; *** significant at P ≥ 0.001; NS not significant; ¶ P desorbed = f (amount of added P); ‡ Linear response; § Quadratic response

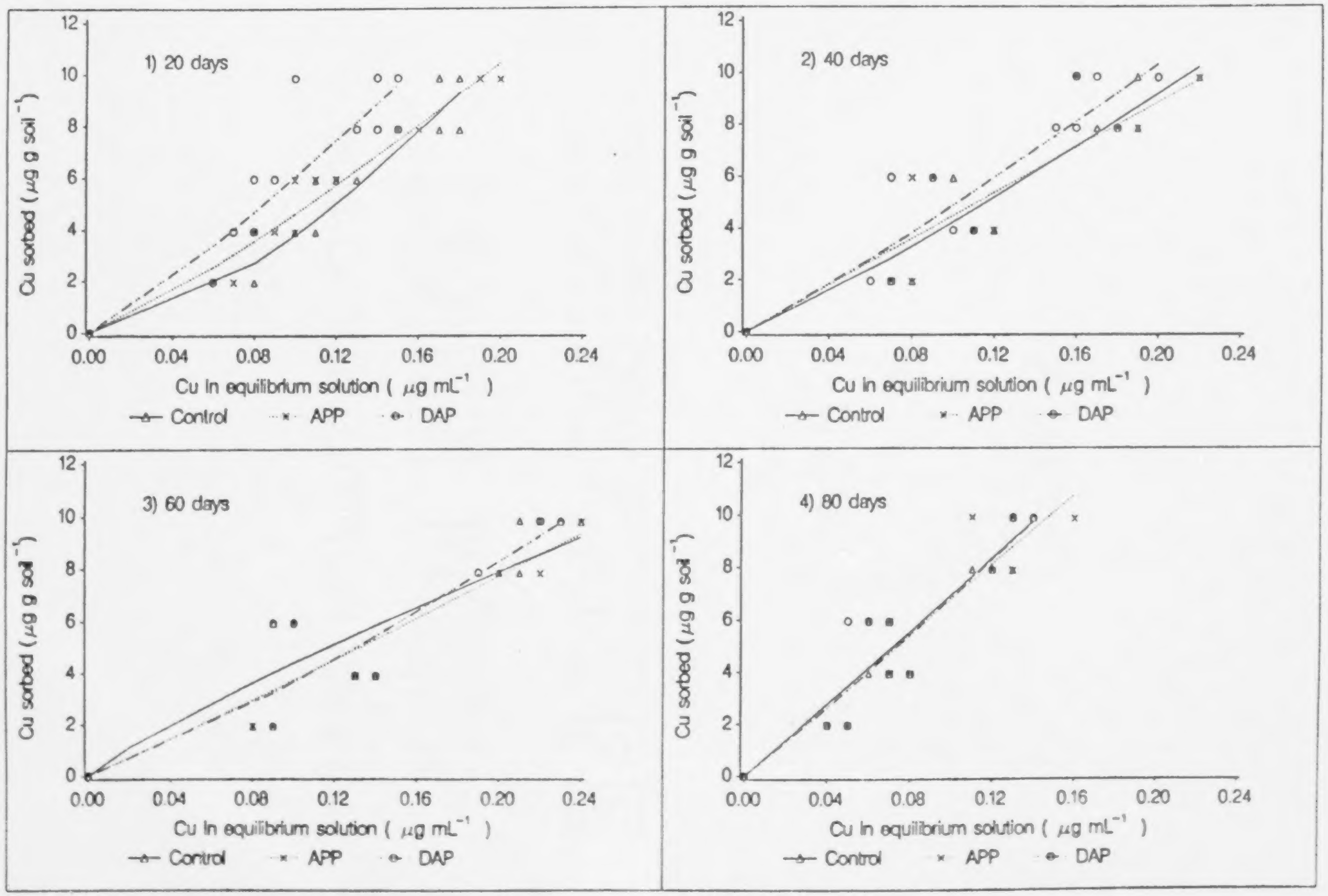


Fig. 4.1 - 4.4 Influence of APP and DAP pretreatments at 15 µg P g soil^{-1} on the sorption of Cu at different times of incubation (individual data points are given)

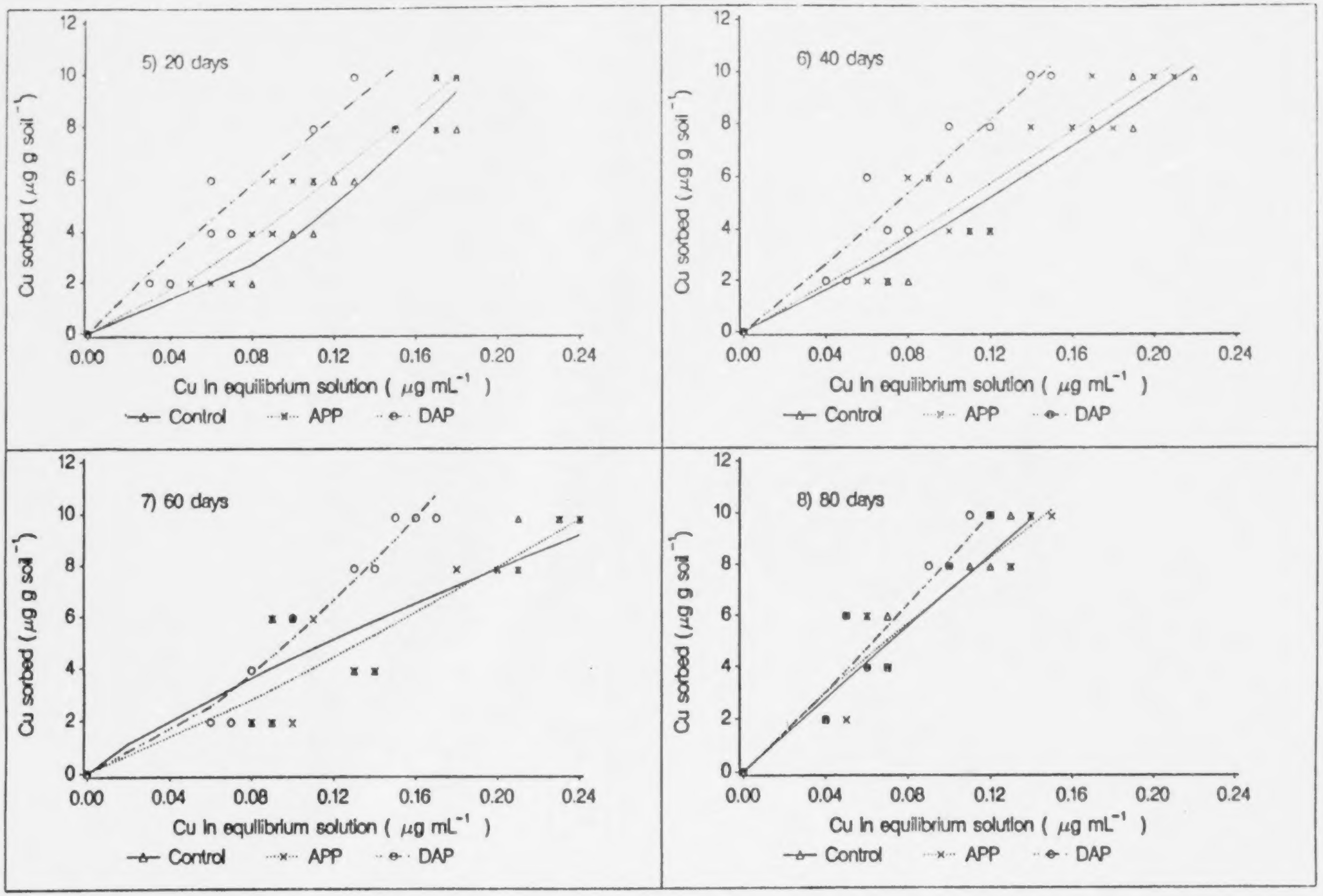


Fig. 4.5 - 4.8 Influence of APP and DAP pretreatments at 30 μg P g soil^{-1} on the sorption of Cu at different times of incubation (individual data points are given)

4. 5 REFERENCES

Asher, L.E., and B. Bar-Yosef. 1982. Effects of pyrophosphate, EDTA and DTPA on zinc sorption by montmorillonite. Soil Sci. Soc. Am. J. 46: 271-276.

Barrow, N. J., and T. C. Shaw. 1975. The slow reactions between soil and anions. 2 . Effect of time and temperature on the decrease in phosphate concentration in the soil solution. Soil Sci. 119:167-177.

Barrow, N. J. 1983. A mechanistic model for describing the sorption and desorption of phosphate by soil. J. Soil Sci. 34: 733-750.

Barrow, N.J. 1991. Testing a mechanistic model X1. The effects of time and of level of application on isotopically exchangeable phosphate. J. Soil Sci. 42: 277-288.

Bolan, N.S., N. J. Barrow, and A. M. Possner. 1985. Describing the effect of time on the sorption of phosphate by iron and aluminum hydroxides. J. Soil Sci. 36: 187-197

Boyd, S. A., L. E. Sommers, D. W. Nelson, and D. K. West. 1981. The mechanism of Cu(II) binding by humic acid: An electron spin resonance study of a Cu (II)-humic acid complex and some adducts with nitrogen donors. Soil Sci. Soc. Am. J. 45: 745-749.

Bruemmer, G. W., J. Gerth, and K. G. Tiller. 1988. Reaction kinetics of the adsorption and desorption of Ni, Zn and Cd by goethite. 1. Adsorption and diffusion of metals. J. Soil Sci. 39: 37-52.

Clark, C.J., and M. B. McBride. 1984. Chemisorption of Cu(II) and Co(II) on allophane and imogolite. Clays Clay Miner. 32: 300-310.

Clark, C. J., and M. B. McBride. 1985. Adsorption of Cu(II) by allophane as affected by phosphate. Soil Sci. 139: 412-421.

Dick, R.P., and M. A. Tabatabai. 1987. Factors affecting hydrolysis of polyphosphates in soils. Soil Sci. 143: 97-104

Elkhatib, E. A., and J. L. Hern. 1988. Kinetics of phosphorus desorption from Appalachian soils. Soil Sci 145: 222-229.

Helyar, K. R., D. N. Munns, and R. G. Burau. 1976. Adsorption of phosphate by gibbsite II. Formation of a surface complex involving divalent cations. J. Soil Sci. 27: 315-323.

Holford, I.C.R., and G. E. G. Mattingly. 1975. The high- and low-energy phosphate adsorbing surfaces in calcareous soils. J. Soil Sci. 26: 407-417.

Holford, I.C.R., R. W. M. Wedderburn, and G. E. G. Mattingly. 1974. A Langmuir two-surface equation as a model for phosphate adsorption by soils. J. Soil Sci. 25: 242-255.

Kafkafi, U., B. Bar-Yosef, R.Rosenberg, and G. Sposito. 1988. Phosphorus adsorption by kaolinite and montmorillonite: II. Organic anion competition. Soil Sci. Soc. Am. J. 52: 1585-1589.

Karathanasis, A.D., F. Adams, and B. F. Hajek. 1983. Stability relationships in kaolinite, gibbsite and Al-hydroxy interlayered vermiculite in soil. Soil Sci. Soc. Am. J. 47: 1247-1251.

Kittrick, J.A., and M. L. Jackson. 1956. Electron-microscope observations of the reactions of phosphate with minerals,leading to a unified theory of phosphate fixation in soils. J. Soil Sci. 7:81-92.

McBride, M.B. 1982. Cu adsorption characteristics of aluminum hydroxide and oxy-hydroxides. Clays Clay Miner. 30: 21-28.

McBride, M. B. 1985a. Sorption of copper(II) on aluminum hydroxide as affected by phosphate. Soil Sci. Soc. Am. J. 49: 843-846.

McBride, M.B. 1985b. Influence of glycine on Cu^{2+} adsorption by microcrystalline gibbsite and boehemite. Clays Clay Miner. 33: 397-402.

Naidu, R., J. K. Syers, R.W. Tillman, and J.H. Kirkman. 1990. Effect of liming and added P on charge characteristics of acid soils. J. Soil Sci. 41: 157-164.

Pardo, M. T., and M. E. Guadalix. 1990. Phosphate sorption in allophanic soils and release of sulphate, silicate and hydroxyl. J. Soil Sci. 41: 607-612.

Pierzynski, G.M., T. J. Logan, S. J. Traina, and J. M. Bigham. 1990. Phosphorus chemistry and mineralogy in excessively fertilized soils: Descriptions of phosphorus-rich particles. Soil Sci. Soc. Am. J. 54: 1583-1589.

Rajan, S.S.S., and R. L. Fox. 1972. Phosphate adsorption by soils. 1. Influence of time and ionic environment on phosphate adsorption. Communi. Soil Sci. Plant Anal. 3: 493-504.

SAS Institute Inc. 1987. SAS/STAT guide for personal computers. Version 6 Edition, Cary, N. C: SAS Institute Inc.

Sibanda, H. M., and S.D. Young. 1986. Competitive adsorption of humus acids and phosphate on goethite, gibbsite and two tropical soils. J. Soil Sci. 37: 197-204.

Subbarao,Y.V., R. Ellis Jr., G. M. Paulsen, and J. V. Paukstelis. 1977. Kinetics of pyro- and tripolyphosphate hydrolysis in the presence of corn and soya bean roots as determined by NMR Spectroscopy. Soil Sci. Soc. Am.J. 41: 316-318.

Syers, J.K., M. G. Browman; G. W. Smillie, and R.B. Corey. 1973. P sorption by soils evaluated by the Langmuir adsorption equation. Soil Sci. Soc. Am. Proc. 37: 358-363.

Veith, J. A., and G. Sposito. 1977. Reactions of alumino-silicates, aluminium hydrous oxides and aluminum oxide with o-phosphate: the formation of X-ray amorphous analogs of variscite and montebrasite. Soil Sci. Soc. Am. J. 41: 870-876.

Chapter 5

KINETICS OF PHOSPHORUS AND COPPER SORPTION: INFLUENCE OF ORTHOPHOSPHATE AND POLYPHOSPHATE

5.1 INTRODUCTION

Adsorption isotherm studies provide information on the quantity of adsorbate retained and its partition between solution and the adsorbent surface, but do not contribute to the understanding of adsorption dynamics. In contrast, reaction rates and other information from kinetic studies provide clues to the adsorption mechanisms and complement the data gathered from sorption isotherm studies. Use of appropriate rate constants for the calculation of activation energy, activation enthalpy and entropy is an added advantage of kinetic studies (Moore, 1982). These functions can be used to explain the ion retention process in soil instead of using the constants from the traditional adsorption isotherm equations (Evans and Jurinak, 1976; Sparks and Jardine, 1981).

Kinetics of Cu sorption and desorption are important to the understanding of its release and subsequent availability to plants. Earlier sorption studies indicated the influence of orthophosphate and polyphosphate on the sorption of Cu (Chapter 3 and 4). However little is known about the rates of Cu sorption in the presence of different forms of P. For an adequate explanation of our earlier studies, we need to know the rate at which Cu interacts with the phosphated surfaces. Although kinetics of orthophosphate sorption has received considerable attention (Kuo and Lotse, 1974; Evans and Jurinak, 1976; Ryden et al., 1977, Barrow et al., 1981; Shang et al., 1990), there is little information on the kinetics of Cu sorption (Bunzel et al., 1976), particularly on the different phosphated surfaces, and the kinetics of polyphosphate sorption. Since the sorption behaviour of Cu was influenced by pretreatment with different forms of P (Chapter 3 and 4), the kinetics of Cu sorption may also be affected by the pretreatment of soil with different P sources. Therefore the objective of the study was to investigate the kinetics of P and Cu sorption as influenced by ammonium polyphosphate (APP) and diammonium orthophosphate (DAP).

5.2 THEORY

In soil, sorption of ions depends on the ion activity in solution and availability of sorption sites. Depletion of solutes from solution at low concentration results from sorption, and so the kinetics of depletion of added Cu and P from solution are taken as indices of their sorption kinetics. A typical adsorption isotherm can be divided into three regions: 1) a low concentration region in which sorption depends on adsorbate activity in solution 2) a high concentration region in which sorption is dependent on the availability of binding sites and 3) an intermediate region in which sorption is affected by site and adsorbate availability. The first order kinetic equation is valid in region 1 and 3. However it is advantageous to work in the region 1 because the adsorbate activity is easy to measure compared to the measurement of site availability (Harter, 1990). The integrated form of the first order kinetic equation (Moore, 1982) is

$$\ln C_t = \ln C_o + kt \qquad [5.1]$$

where: t is time (h)

C_o is adsorbate concentration at time 0

C_t is adsorbate concentration at time t

k is rate constant (h^{-1})

Rate constants determined at different temperature are used to calculate the activation energy based on the Arrhenius equation

$$k = A\ e^{-Ea/RT} \qquad [5.2]$$

where: A is a constant (h^{-1})

Ea is activation energy ($KJ\ mol^{-1}$)

R is universal gas constant ($8.314 \times 10^{-3}\ KJ\ mol^{-1}\ K^{-1}$)

T is absolute temperature (K)

A plot of $\ln k$ versus $1/T$ would result in a linear relationship with the slope equal to $-Ea/R$, and intercept = $\ln A$.

Activation enthalpy and entropy can then be calculated from the following relationships (Sparks, 1989)

$$H = Ea - RT \qquad [5.3]$$

$$k = k_B T/h\ (\ e^{(S/R)-(H/RT)}) \qquad [5.4]$$

where: k_B is Boltzman constant (1.381×10^{-26} KJ K^{-1})

h is Planck constant (6.626×10^{-37} KJ s^{-1})

S is entropy of activation

H is enthalpy of activation

5.3 MATERIALS AND METHODS

A copper deficient soil sample was used and it was the same soil as that in Chapter 2 to 4. Some of the physical and chemical properties are given in Table 2.1. Kinetics of Cu sorption was studied on soil with APP and DAP pretreatments, as well as with no pretreatment (control). Phosphorus pretreatment for Cu sorption was conducted by incubating 200 g air dried, sieved (< 1 mm) soil samples (in two replications for 48 h at 295 K) with APP or DAP at 25 millimol P kg $soil^{-1}$ dissolved in water. Soil moisture content was maintained at 60 per cent of the moisture held at field capacity (0.033 MPa) using deionized water. Phosphorus (APP and DAP) sorption kinetics were studied in soil samples (in duplicate) without any pretreatment. Equilibrating solutions of P (APP and DAP at 0.5 millimol P L^{-1}) and Cu ($CuSO_4 \cdot 5H_2O$ at 0.5 millimol Cu L^{-1}) were made in 0.03 M $KClO_4$ solution. Solution pH was adjusted to 5.80 ± 0.02 with dilute KOH or $HClO_4$.

Kinetics of P and Cu sorption were measured by mixing suspensions (2.5 g soil with 25 mL of solution containing Cu or P) for different times and temperatures on a reciprocating shaker kept inside an incubator maintained at constant temperature. The mixing times were 0.25, 0.5, 1, 2, 4, 8, 16 and 24 h and the temperatures were 281, 291, and 301 K. The treatments at each time for Cu sorption were: Control (soil without any pretreatment), Pretreated with APP, Pretreated with DAP. There were six experimental units at each time at each temperature for Cu sorption kinetics, and four for P sorption kinetics. All solutions and soil samples were equilibrated with the particular reaction temperature before the commencement of the sorption study. Suspensions at the end of each equilibration were centrifuged for 15 min. at 22000 RPM, and filtered through a Whatman No. 42 filter paper. The concentration of total P and Cu in solution was determined by Inductively Coupled Plasma Atomic Emission Spectroscopy.

One step vs two step sorption mechanisms for Cu and P

Kinetic equations for various time periods (0.25 to 1 h, 2 to 8 h, 0.25 to 4 h, 0.25 to 8 h) for all treatments at all temperatures were generated for identifying a two step reaction, if any, for Cu sorption kinetics. When a treatment followed the first order kinetics at two reaction periods (0.25 to 1 h and 2 to 8 h) at a specific temperature, then the value of k for those two periods were compared for identifying the reaction steps for that treatment (reaction period with higher k will be faster than the one with lower k). In my experiment not all treatments followed first order kinetics at both reaction periods at all temperatures. There could be two reasons for this[1]: 1) most of the added Cu was sorbed during 0.25 h period; 2) insufficient data points (time intervals) were taken.

Rate constants can tell only about the speed of a reaction. Activation energy, H and S are needed for understanding the sorption mechanisms. However, calculation of Ea, H and S is possible when k for a particular time interval is significant[2] at different selected temperatures. For all treatments in my experiment, k during the two time intervals was not significant at all temperatures, and therefore it is not possible to calculate Ea, H and S at those two time intervals[3]. So it is not reasonable to separate the sorption mechanisms (based on Ea, H and S) during 0.25 to 1 h and 2 to 8 h for a particular treatment using my data. However whenever possible the rate of Cu sorption (based on k) for a particular treatment during the two time intervals was compared at certain temperatures (temperature at which the two reaction periods followed first order kinetics).

---

[1] Personal communication with S. A. Abboud, Alberta Research Council, Edmonton

[2] k is said to be significant when the reaction during a specific time interval can be represented by the first order kinetic equation based on R^2

[3] Refer Equations 5.2 -5.4

During 0.25 to 4 h period, all three treatments followed the first order kinetics for Cu sorption (based on R^2 value), and so, this reaction period was selected for calculating Ea, H and S, and for comparing various treatments in the Cu sorption study[4]. This procedure does not rule out the possibility of the fast and slow reaction steps (based on k) observed for some treatments at certain temperatures[5].

For P sorption, kinetic equations for 0.25 to 1 h and 2 to 8 h were used to determine if there were different sorption mechanisms. As for Cu sorption, k value for P sorption during a particular reaction time was not significant at all temperatures and therefore it is not possible to conclude that there are different sorption mechanisms during the two time intervals. However k for all treatments was significant during 0.25 to 8 h period at all temperatures. So this time interval was taken for treatment comparison.

Parameters (k and Ct) of the kinetic equation were calculated using the PROC REG in SAS (SAS Institute, 1987).

5.4 RESULTS

5.4.1 KINETICS OF Cu SORPTION

The solution concentration of Cu decreased with time of reaction up to 4 h in all treatments (Fig. 5.1- 5.3). In the last two or three reaction periods (8, 16 and 24 h; Appendix 22), solution concentration of Cu increased and the data were not used in subsequent calculations. Pretreatment with APP resulted in the highest solution concentration of Cu in all reaction periods, except the 0.25 h at 301 K (Fig. 5.3) where the control had the maximum concentration. However, unlike the sorption of Cu[6] after the P pretreatments, solution concentration decreased markedly from 0.50 h onwards in the control treatment, and it tended to maintain the lowest mean concentration at all temperatures (Fig. 5.1-5.3).

---

[4] Personal communication with S. A. Abboud, Alberta Research Council, Edmonton

[5] Refer section 5.4.1 (second paragraph)

[6] Depletion of Cu from the equilibrium solution is taken as an index of Cu sorption (refer section 5.2)

At all temperatures, the control treatment followed first order kinetics during 0.25 to 1 h (Table 5.1). At 281 and 291 K, DAP pretreatments had significant k at both time periods. In APP pretreatments, k was significant during 0.25 to 1 h at 291 and 301 K, and during 2 to 8 h at 281 K. Based on the magnitude of k, Cu sorption during 0.25 to 1 h reaction period was identified as a fast reaction step in the control at 281 and 301 K, and the later 2 to 8 h period as a slow reaction step (Table 5.1). For DAP pretreatments, there was a fast reaction step during 0.25 to 1 h at 281 and 291 K, and a slow reaction step during 2 to 8 h. Comparison of the speed of Cu sorption in APP pretreatments during the two reaction periods was not possible at any of the three temperatures.

During 0.25 h to 4 h period, all the treatments followed first order kinetics (based on R^2), and this reaction period was used for further discussion. Rate constants for Cu sorption were maximum in the control (Table 5.1). With P pretreatment, the largest k for Cu sorption was with DAP at each temperature. There was an increase in k with temperature in all treatments. Copper sorption in the control had the lowest Ea, and sorption after APP pretreatment had the highest Ea (Table 5.2, Appendix 23). Highest enthalpy of activation was for the sorption of Cu in the APP pretreated soil and it was least for the control (Table 5.2). The entropy of activation was more negative in the control than in the other treatments (Table 5.2). Activation entropy for Cu sorption was less negative with APP than with DAP pretreatment.

5.4.2 KINETICS OF P SORPTION

The concentration of P in solution was dependent on the reaction time, temperature and the form of added P (Fig. 5.4-5.6). In all the reaction times and temperatures, the P concentration in solution was greater for DAP than for APP. The solution concentration decreased gradually with time up to 8 h of reaction and after which there was not a clear trend (16 and 24 h; Appendix 24).

APP treatments followed first order kinetics during the two time periods (0.25 to 1 h and 2 to 8 h) at 281 and 301 K, and DAP treatments at 281 and 291 K. Rate constants for APP sorption was higher during 0.25 to 1 h than during 2 to 8 h at 281 and 301 K (Table 5.3). The k for DAP sorption was higher during 0.25 to 1 h than at 2 to 8 h at 281 and 291 K.

Phosphorus sorption up to 8 h followed first order kinetics (based on R^2) at all temperatures, and this time period was used for further discussion. Rate constants in both the treatments increased with temperature, and the increase was more for a 10 K rise in temperature from 291 K than from 281 K. Sorption of APP had higher rate constants than DAP at all temperatures.

The activation energy for P sorption was greater with DAP compared to APP (Table 5.4, Appendix 23). The activation enthalpy was higher for DAP than for APP at all temperatures. When the form of added P was APP, the activation entropy was more negative than when it was DAP.

5.5 DISCUSSION

Nearly all of the Cu sorption was completed in the first 0.25 h and the kinetics of sorption during this short period was difficult to measure with a batch technique. Similar fast sorption kinetics for Cu sorption were reported by Harter and Lehmann (1983) and Inskeep and Baham (1983). Copper sorbed during the fast reaction step (0.25 to 1 h) in the control and DAP pretreatment at certain temperatures might have gone to the high affinity sites, and that sorbed during the slow reaction step (2 to 8 h) to the low affinity sites in soil. A higher k (during 0.25 to 4 h) for Cu depletion in the control treatment indicates a faster sorption of Cu than after P pretreatment. However rate constants alone can not provide information about the sorption mechanisms (Skopp, 1986). Activation energy, H and S are needed for explaining different sorption mechanisms. Calculation of Ea, H and S for the two reaction steps identified in the control and in the DAP pretreatment is not possible because the k for a particular time interval was not significant at all temperatures. Hence verification of different sorption mechanisms at 0.25 to 4 h, and at 2 to 8 h was not possible. However, activation energy, enthalpy and entropy during 0.25 to 4 h reaction period shows the presence of different sorption mechanisms or sorption sites in different treatments.

Activation energy (0.25 to 4 h) is the minimum energy needed to start the reaction and varies inversely with reaction rate. The lowest activation energy for Cu sorption, observed in the control treatment, indicated that the energy needed to sorb Cu in a soil without added P was lower than the sorption of Cu after P pretreatment.

Sparks (1989) suggested that Ea values less than 42 KJ mol^{-1} were an indication of diffusion controlled processes whereas higher Ea indicated chemical processes. Based on this critical value of Ea, it is postulated that the sorption of Cu in soil with or without P pretreatment is a diffusion controlled process. Harter and Lehmann (1983) attributed the fast sorption of Cu immediately after its addition to exchange reactions. Generally exchange reactions are fast and diffusion controlled. Copper can exchange most of the cations from the exchange sites because of its high affinity for the adsorbing sites.

The high Ea for Cu after P pretreatment indicated the possibility of ternary complex formation or direct complexation with the adjacent phosphate anions, particularly with DAP pretreatment. Between the two P sources, the greater Ea for Cu sorption with APP pretreatment suggests that the sorption of Cu on the orthophosphated surface was faster than on the polyphosphated surface.

The enthalpy of activation is a measure of the energy barrier that must be overcome by the reacting molecules (Sparks and Jardine, 1981). The low activation enthalpy (0.25 to 4 h) obtained in the control at all temperatures indicated that the energy barrier for Cu sorption was low and this increased the rate and amount of sorption. The higher activation enthalpy with APP pretreatment relative to DAP pretreatment suggested that the energy barrier for Cu sorption was lower with orthophosphate than with polyphosphate. This caused a higher rate and amount of sorption of Cu in DAP pretreated soil.

The more negative activation entropy values (0.25 to 4 h) in the control treatment indicates the formation of a system with more ordered molecular arrangement in less time. In the case of APP, the less negative entropy values obtained as compared to DAP suggests the possibility of formation of a loosely bound structure following APP pretreatment. When the system is more random, desorption will be faster. Therefore, a greater proportion of the sorbed Cu can be desorbed when the soil is pretreated with APP than when pretreated with DAP or without any added P. When Cu is added to a soil (without any pretreatment), the chances of getting high affinity sites will be greater. This results in a more stable surface complex formation.

The rate constants for P sorption indicate that APP, when added at 0.5 millimol P L^{-1}, was sorbed faster than DAP. Value of k at the two time intervals (0.25 to 1 h and 2 to 8 h) suggests a faster sorption of APP during 0.25 to 1 h than during 2 to 8 h at 281 and 301 K. DAP sorption was faster (based on k) during 0.25 to 1 h than during 2 to 8 h at 281 and 291 K.

Activation energy for the sorption of APP and DAP (during 0.25 to 8 h) were lower than 42 KJ mol^{-1} and this indicated that the sorption process was a diffusion controlled process (Sparks, 1985). Kuo and Lotse (1974) reported a low activation energy of 8 KJ mol^{-1} for the adsorption of orthophosphate on iron minerals. In the present experiment, the relatively low activation energy for APP sorption resulted in a faster rate of sorption compared to DAP. In addition, the low energy barrier for the polyphosphate sorption was reflected in the low activation enthalpy values, resulting in more sorption. The more negative entropy values for the sorption of polyphosphate was another indication of a system with more ordered structure formation in a short period leading to a fast sorption when added at 0.5 millimol P L^{-1}.

A comparison of k, Ea, activation enthalpy and activation entropy for P and Cu sorption reveals that the sorption of Cu in soil without P pretreatment was the fastest sorption process followed by the sorption of APP and then DAP. When APP was added at low concentration, the high flexibility of the condensed phosphates may enable it to coordinate with surface cations leading to greater sorption, and the direct complex formation with metals in solution might have been negligible because of the low concentration. Higher sorption of linear polyphosphates than orthophosphates on the soil solids was also reported by Xie and MacKenzie (1990), Blanchar and Hossner (1969), and Sutton and Larsen (1964).

The low activation enthalpy and more negative entropy values for the sorption of Cu in soil without P pretreatment implies that there would be a slow desorption of the sorbed Cu when added at 0.5 millimol Cu L^{-1}.

5.6 SUMMARY AND CONCLUSIONS

A major part of the added Cu and P was sorbed in the initial reaction periods. Copper sorption was slowed in soil when pretreated with P. Pretreatment of soil with APP resulted in a lower amount and slower rate of Cu sorption compared to the pretreatment with DAP. In the control and DAP pretreatments sorption of Cu was faster during 0.25 to 1 h than during 2 to 8 h. Activation entropy for Cu sorption was more negative in DAP pretreated soil than in APP pretreated soil. However Ea and activation enthalpy were lower for the Cu sorption following pretreatment with DAP than with APP. Activation energy and other thermodynamic functions for P sorption show that APP was sorbed faster than DAP.

Table 5.1 Influence of APP and DAP pretreatments on the rate constant (k) for Cu depletion during different time intervals.

Treatments	Temperature (K) 281	291	301
		h^{-1}	
0.25 to 1 h			
Control	0.4107	0.4199	0.4569
APP	*NS	0.0723	0.0289
DAP	0.0809	0.1661	NS
2 to 8 h			
Control	0.0249	NS	0.0444
APP	0.0149	NS	NS
DAP	0.0127	0.0217	NS
0.25 to 4 h			
Control	0.0981	0.1483	0.1535
APP	0.0237	0.0617	0.0718
DAP	0.0368	0.0682	0.0803
0.25 to 8 h			
Control	NS	0.0737	0.0823
APP	0.0197	NS	NS
DAP	0.0213	NS	NS

* k was not significant during that time interval

Table 5.2 Influence of APP and DAP pretreatments on the activation energy (Ea), activation enthalpy and negative activation entropy of Cu depletion for 0.25 to 4.00 h reaction period.

	Temperature (K)			
Treatments	281	291	301	Ea KJ mol^{-1}
Activation enthalpy (KJ mol^{-1})				
Control	13.54	13.46	13.38	15.88
APP	36.76	36.76	36.68	39.18
DAP	25.26	25.18	25.10	27.60
Activation entropy (J mol^{-1})				
Control	-216	-214	-216	
APP	-148	-141	-145	
DAP	-182	-181	-183	

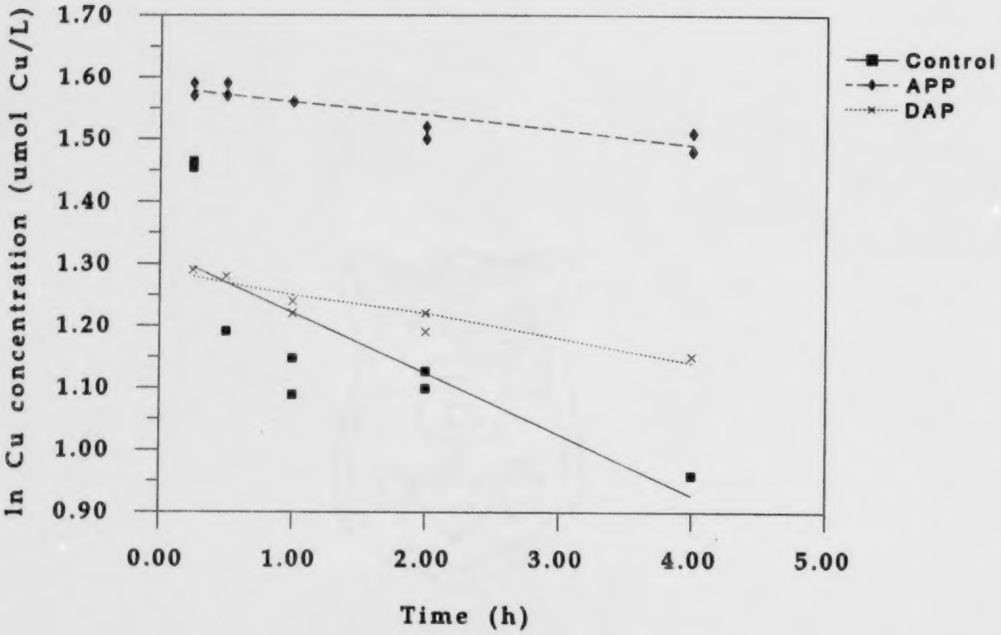
Table 5.3 Influence of P sources on the rate constant (k) for the depletion of P from solution at different time intervals

Treatments	Temperature (K) 281	 291	 301
	h^{-1}		
0.25 to 1 h			
APP	0.0800	•NS	0.0840
DAP	0.0940	0.1620	NS
2 to 8 h			
APP	0.0190	0.0170	0.0240
DAP	0.0120	0.0110	NS
0.25 to 8 h			
APP	0.0276	0.0280	0.0381
DAP	0.0230	0.0273	0.0365

• k was not significant during that time interval

Table 5.4 Influence of P sources on the activation energy (Ea), activation enthalpy, and negative activation entropy for the depletion of P from solution in 0.25 to 8 h

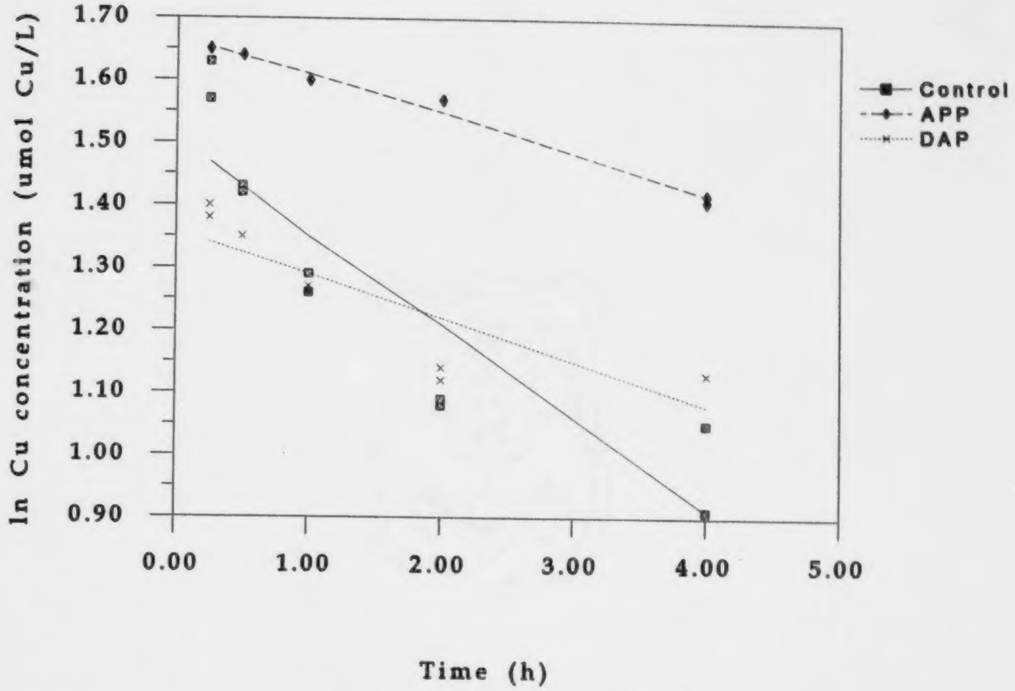
	Temperature (K)			
Treatments	281	291	301	Ea KJ mol^{-1}
Activation enthalpy **(KJ mol^{-1})**				
APP	8.87	8.79	8.71	11.21
DAP	13.80	13.72	13.64	16.14
Activation entropy **(J mol^{-1})**				
APP	-243	-244	-243	
DAP	-227	-227	-227	



Regression equations

Control	$\ln C_t = 1.319\ (0.052) - 0.0981\ (0.012)t$	$R^2 = 0.66$
APP	$\ln C_t = 1.584\ (0.009) - 0.0237\ (0.004)t$	$R^2 = 0.80$
DAP	$\ln C_t = 1.289\ (0.009) - 0.0368\ (0.004)t$	$R^2 = 0.91$

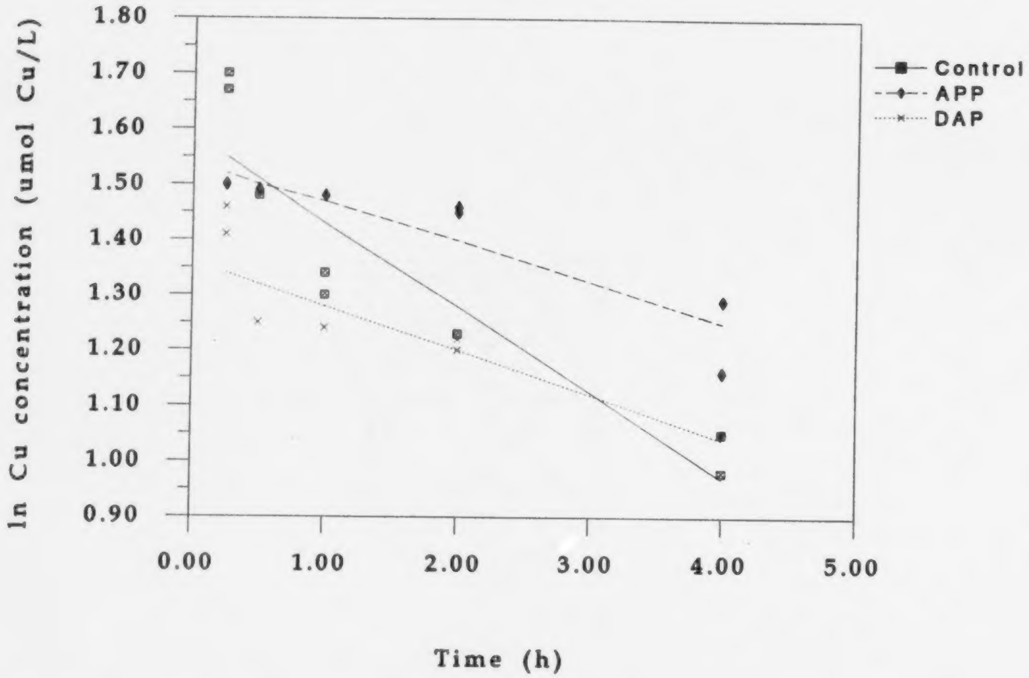
Fig. 5.1 Rate of Cu depletion at 281 K as influenced by the P pretreatments (individual data points are given)



Regression equations

Control	$\ln C_t = 1.5023\ (0.054) - 0.1483\ (0.026)t$	$R^2 = 0.80$
APP	$\ln C_t = 1.6690\ (0.006) - 0.0617\ (0.003)t$	$R^2 = 0.98$
DAP	$\ln C_t = 1.3580\ (0.029) - 0.0682\ (0.014)t$	$R^2 = 0.75$

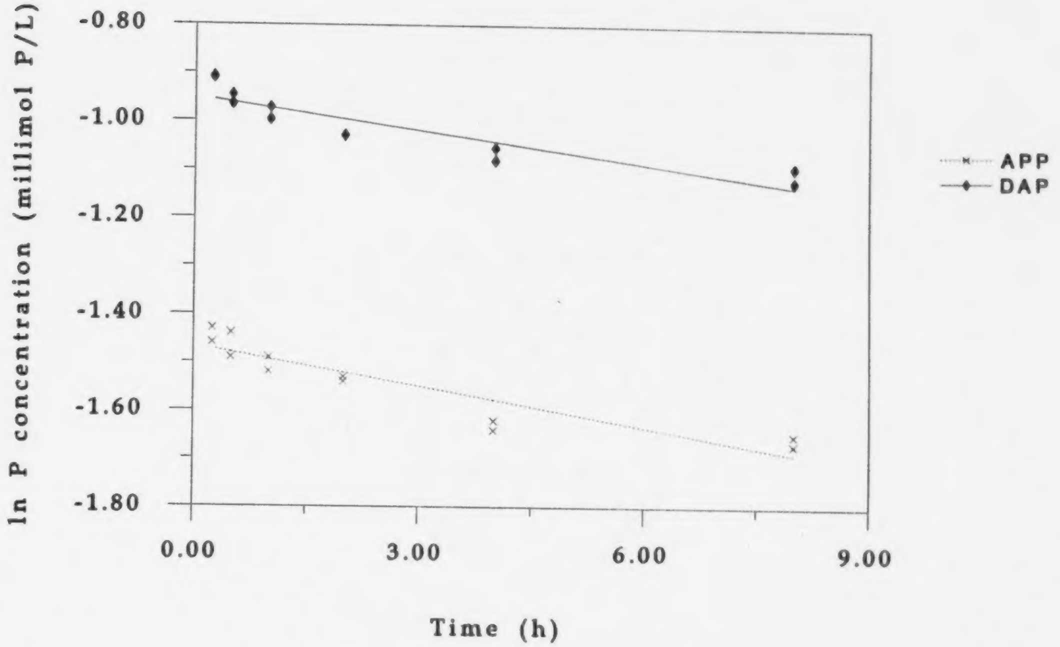
Fig. 5.2 Rate of Cu depletion at 291 K as influenced by the P pretreatents (individual data points are given)



Regression equations

Control	$\ln C_t = 1.5839\ (0.046) - 0.15350\ (0.022)t$	$R^2 = 0.86$
APP	$\ln C_t = 1.5398\ (0.023) - 0.01718\ (0.011)t$	$R^2 = 0.84$
DAP	$\ln C_t = 1.3617\ (0.031) - 0.08030\ (0.015)t$	$R^2 = 0.78$

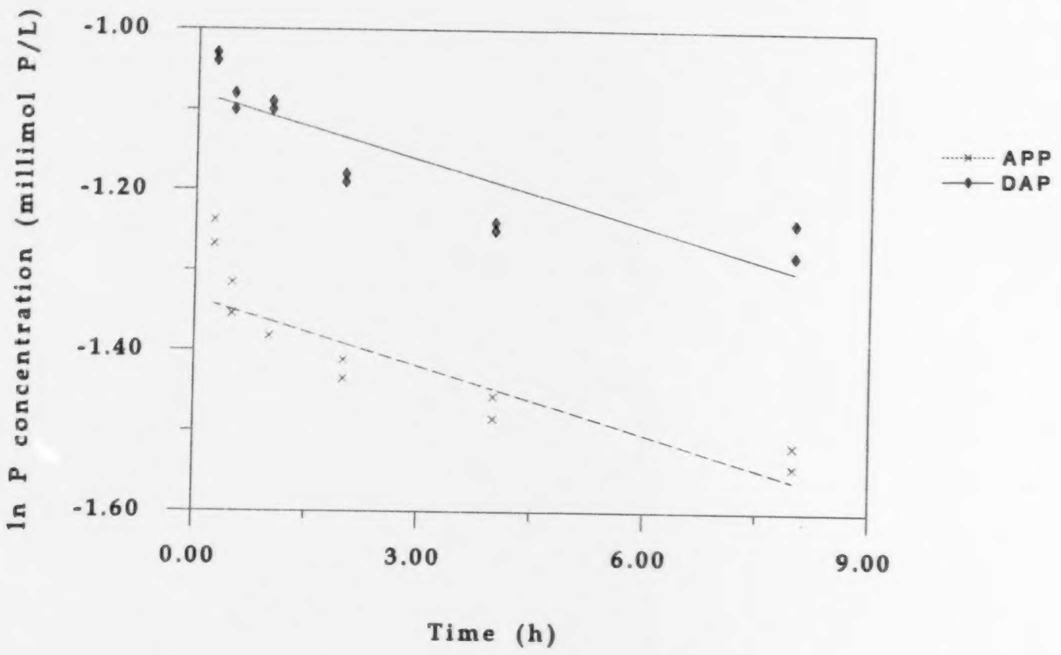
Fig. 5.3 Rate of Cu depletion at 301 K as influenced by the P pretreatments (individual data points are given)



Regression equations

APP	$\ln C_t = -1.4661\ (0.014) - 0.0276\ (0.003)t$	R2 = 0.85
DAP	$\ln C_t = -0.9505\ (0.023) - 0.0227\ (0.001)t$	R2 = 0.79

Fig. 5.4 Rate of P depletion at 281 K as influenced by the P pretreatments (individual data points are given)

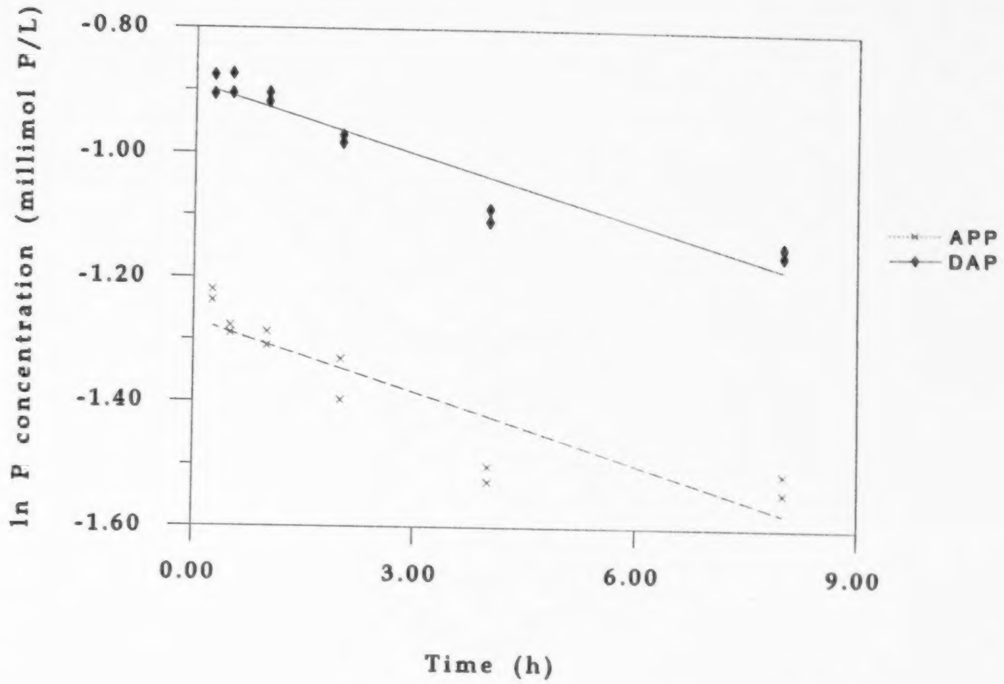


Regression equations

APP $\ln C_t = -1.3350\ (0.012) - 0.0281\ (0.001)t$ $R^2 = 0.77$

DAP $\ln C_t = -1.0803\ (0.019) - 0.0273\ (0.005)t$ $R^2 = 0.75$

Fig. 5.5 Rate of P depletion at 291 K as influenced by the P pretreatments (individual data points are given)



Regression equations

APP $\ln C_t = -1.270\ (0.022) - 0.0381\ (0.004)t$ $R^2 = 0.81$

DAP $\ln C_t = -0.891\ (0.014) - 0.0365\ (0.004)t$ $R^2 = 0.90$

Fig. 5.6 Rate of P depletion at 301 K as influenced by the P pretreatments (individual data points are given)

5.7 REFERENCES

Barrow , N. J. , L. Madrid, and A.M. Posner. 1981. A partial model for the rate of adsorption and desorption of phosphate by goethite. J. Soil Sci. 32: 399-407.

Blanchar, R. W., and L.R. Hossner. 1969. Hydrolysis and sorption reactions of orthophosphate, pyrophosphate and tripolyphosphate anions added to an Elliot Soil. Soil Sci. Soc. Am. Proc. 33: 141-144.

Bunzel, K., W. Schmidt, and B. Sansoni. 1976. Kinetics of ion exchange in soil organic matter. IV. Adsorption and desorption of Pb^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+} and Ca^{2+} by wheat. J. Soil Sci. 27: 32-41.

Evans, R. L., and J. J. Jurinak. 1976. Kinetics of phosphate release from a desert soil. Soil Sci. 121. 205-211.

Harter, R.D., and R. G. Lehmann. 1983. Use of kinetics for the study of exchange reactions in soils. Soil Sci. Soc. Am. J. 47: 666-669.

Harter, R.D. 1990. Interpreting the kinetics of ion sorption by soils. p II.22-27. *In* 14th International Congress of Soil Sci. Transactions, Vol. II, Commission II, International Soc. Soil Sci., Kyoto, Japan, August,1990.

Inskeep, W. P., and J. Baham. 1983. Adsorption of Cd (II) and Cu (II) by Na-montmorillonite at low surface coverage. Soil Sci. Soc. Am. J. 47: 660-665.

Kuo, S, and E. G. Lotse. 1974. Kinetics of phosphate adsorption and desorption by hematite and gibbsite. Soil Sci. 116: 400-406.

Moore, W.J. 1982. Basic physical chemistry. Prentice-Hall Inc. New Jersey.

Ryden, J. C., J. R. McLaughlin, and J. K. Syers. 1977. Time- dependent sorption of phosphate by soils and hydrous ferric oxides. J. Soil Sci. 28: 585-595.

SAS Institute Inc. 1987. SAS/STAT guide for personal computers. Version 6 Edition, Cary, N. C. SAS Institute Inc.

Shang, C., P.M. Huang, and J.W. B. Stewart. 1990. Kinetics of adsorption of organic and inorganic phosphates by short- range ordered precipitate of aluminum. Can. J. Soil Sci. 70: 461-470.

Skopp, J. 1986. Analysis of time-dependent chemical processes in soils. J. Environ.

Qual. 15: 205-213.

Sparks, D.L.,and P. M. Jardine. 1981.Thermodynamics of potassium exchange in soil using a kinetic approach. Soil Sci. Soc. Am. J. 45. 1094-1099.

Sparks, D.J. 1985. Kinetics of ionic reactions in clay minerals and soils. Adv. Agron. 38: 231-266.

Sparks, D.J. 1989. Kinetics of soil chemical processes. Academic Press, Inc New York

Sutton, C. D., and S. Larsen. 1964. Pyrophosphate as a source of P for plants. Soil Sci. 97: 196-201.

Xie, R. J. , and A. F. MacKenzie. 1990. Sorbed ortho- and pyrophosphate effects on Zn reactions compared in three autoclaved soils. Soil Sci. Soc. Am. J. 54: 744-750.

CHAPTER 6

Cu AND P IN SOIL SOLUTION AND THEIR SOLUBILITY CONTROLLING SOLIDS AS AFFECTED BY P SOURCES

6.1 INTRODUCTION

The bioavailability of Cu and P, and their behaviour in soil are dependant more on their speciation than their total concentration. Chemical species of elements are related to the ionic environment of aqueous solutions. Further, metal species can exist in dissolved form, colloidal form or as precipitates. Determination of ion activities in soil solution will help in the prediction of solid phases that may control the activities of various elements under specific conditions (Leckie and Davis, 1979). Ion activities can be estimated from the solution concentrations using speciation models like GEOCHEM (Sposito and Mattigod, 1979).

The availability of added P to current crop, as well as that of the residual P to the succeeding crop, depends on the nature and amount of compounds to which the applied P is converted. Phosphorus is mostly absorbed by plants as primary and secondary orthophosphate ions, and Cu as free ions. Earlier experiments (Chapter 3 and 5) showed higher concentration of solution P with diammonium phosphate (DAP) application than with ammonium polyphosphate (APP). However, the solution Cu was greater when the soil was initially treated with APP than with DAP. Copper and P can form complexes in soil solution and this affects their activities (free ion) and therefore their availabilities to plants. So it is important to understand the activity of Cu-P complexes in soil solution under the influence of APP and DAP. However, no work has been reported in the literature about speciation of Cu in soil solutions in the presence of different P sources. Therefore the objective of the present study was to determine whether the two P sources affected soil solution Cu-P complexes and the solubility controlling solids in the system at different times.

For a complete speciation of Cu in solution, estimation of all inorganic and organic ions in soil solution is required. To simplify my experiment, organic ions were not determined. It was assumed that if Cu-P precipitates were not indicated by the GEOCHEM model when organics were excluded, they would be even less probable if organics, which would lower Cu activity, were included.

6.2 MATERIALS AND METHODS

A Cu deficient soil was used and some of its properties are given in Table 2.1. Air dried soil was sieved (1 mm) and 1.50 kg soil was placed in plastic containers and mixed with P and/or Cu. Ten treatments were applied: APP and DAP at 15 and 30 μg P g soil^{-1} with Cu at 10 μg Cu g soil^{-1} (APP15 +Cu, APP30 +Cu, DAP15 +Cu, DAP30 +Cu), APP alone (APP15 and APP30), DAP alone (DAP15 and DAP30), Cu alone, and a control. Copper was added as $CuSO_4 . 5H_2O$. The compounds were dissolved in water and mixed with soil. Soil moisture content was maintained at 60 per cent of the moisture held at field capacity (0.033 MPa) by adding deionized water. Container lids had aeration holes and the containers with the treated soil were placed in an incubator at 25^0 C for 80 days in a completely randomized design. Each treatment was replicated three times. Soil samples were taken at 20, 40, 60 and 80 days to obtain the saturated soil extracts (soil solution). Thus there were 30 experimental units at each time. Saturated soil pastes were prepared (using a portion of 1.50 kg soil) with deionized water and equilibrated for 24 hours at 25^0 C and the soil solutions were extracted by vacuum using Buchner Funnel and Whatman No. 40 paper. Electrical conductivity and pH of the soil solution were determined immediately after extraction and these solutions were stored at 5^0 C until the determination of total concentration of Cu, Fe, Mn, Zn, Al, Ca, Mg, K, P, S and NO_3^-. These ions, except NO_3^-, were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy; NO_3^- was determined by a Autoanalyser. Total P was taken as total orthophosphate concentration. Analysis of variance at each time (30 experimental units) for pH and ionic strength were done using PROC GLM in SAS (SAS Institute, 1987). The negative logarithms (-log) of total ionic concentration (mean of three replications) were the input values for speciation in the GEOCHEM model (GEOCHEM-PC version 2.0 (Parker et al., 1990) a modified version of GEOCHEM developed by

Sposito and Mattigod, 1979). Solution pH and ionic strength were fixed when the model was run. Ionic strength (I) was calculated from the electrical conductance (E.C.).

$$I = E.C. * 0.013$$ (Griffin and Jurinak, 1973)

Ion activities of Cu^{2+}, $H_2PO_4^-$, Fe^{3+} and Al^{3+} were calculated using GEOCHEM. Since the organic anions are excluded, the free ion activity of Cu (calculated by the model) includes the ionic form of Cu together with all complexes of Cu with unaccounted anions including organics. The ion activities so calculated were compared to the theoretical mineral solubility constants (Lindsay, 1979) with the stability diagrams to determine their solubility controlling solids. The solution ion activity is considered supersaturated relative to a solubility controlling solid if the intersection of the -log of ion activity and pH coordinates fall above the particular mineral isoline, and it is considered undersaturated if these intersection points fall below the isoline. The system is at saturation if the measured ion activity occurs on the mineral isoline.

Since polyphosphates are unstable in soils and eventually convert to orthophosphates, and plant uptake of P is in orthophosphate form, only solution complexes of orthophosphates are discussed. Redox reactions were not considered because the soil was not incubated under saturated condition. A complete discussion of free ion activity of Cu calculated by the model is not possible from my experiment, due to the exclusion of organic anions. However exclusion of organics and other anions will not affect the conclusion that the Cu-P solids (if formed) will limit the activity of Cu in soil solution. Failure to show the presence of Cu-P precipitates when organics and other anions were excluded would imply that such precipitates would be even less likely to form, had those anions been included. Differences among treatments were considered meaningful when there was a 10 fold or greater difference in the activity (mol L^{-1}) values calculated using GEOCHEM.

6.3 RESULTS

6.3.1 COMPOSITION OF SOIL SOLUTION

Soil solution pH of the control treatment at 20 days was higher than other treatments (Fig.6.1 and 6.2). However the difference between control and other treatments disappeared in subsequent time periods. When APP was added at 15 μg P g soil^{-1} (with or without Cu), the pH of the solution tended to be higher compared to other treated soils. In all the treatments there was a gradual decline in pH with time of incubation. At all times of sampling APP added at 30 μg P g soil^{-1} had higher pH than DAP added at 30 μg P g soil^{-1}.

At 20 days, P added at the lower rate and the Cu alone treatment had lower ionic strengths (I) than the control, but when P was added at 30 μg P g soil^{-1}, I was similar to the control (Fig. 6.3 and 6.4). In the last three sampling periods, P treated soils tended to have a higher I than non P treatments (Control, Cu alone). Increasing time of incubation increased the I of solution.

Among the measured anions, NO_3^- had the highest concentration in the saturated soil extract (Table 6.1 - 6.4). Regardless of the P sources, total P content in the saturated soil extract increased with the rate of P application. In the no P treatments (Control and Cu alone) concentration of total soluble P ranged from 5.80 to 12.6 μmol P L^{-1}. Total Cu concentration in the saturated soil extract was low (0.16 to 0.32 μmol Cu L^{-1}). These values of Cu and P were in agreement with Sanders (1982) and Simard et al., (1988). Among the micronutrient cations, Fe had the highest solution concentration. Concentration of Zn in solution was similar to that of Cu.

6.3.2 FREE ION ACTIVITY OF Cu, $H_2PO_4^-$, AND HPO_4^{2-}

Free ion activity of Cu ranged from 0.08 to 0.32 μmol Cu L^{-1} (Table 6.5). These values might be an overestimation because of the exclusion of soluble organics from the model, and so they were not discussed further. The activity of $H_2PO_4^-$ was higher than HPO_4^{2-} (Table 6.5). Simard et al., 1988 also observed higher $H_2PO_4^-$ activity than HPO_4^{2-} activity in soil solutions with similar pH values. In the first three sampling periods, the ion activity of $H_2PO_4^-$ was greater than the control only when both forms of P were added at 30 μg P g soil^{-1}. However at 80 days, all the treatments that received the application of P had higher $H_2PO_4^-$ activity compared to the non-P treatments. Addition of Cu along with APP or DAP did not change the activity of $H_2PO_4^-$

6.3.3 ACTIVITY OF Cu-P COMPLEXES

The activity of Cu-P complexes in solution predicted from the model is not affected by the exclusion of organics, and so the various treatments are compared. The two P sources did not affect the activities of Cu-P complexes in soil solution (Table 6.6).

The activity of $Cu\text{-}H_2PO_4^+$ was higher than $Cu\text{-}HPO_4$ in all the treatments at each time (Table 6.6). There was no difference among the treatments with respect to the activity of $Cu\text{-}H_2PO_4^+$ except at 60 days where the activity was marginally higher when P was added at 30 μg P g soil^{-1} as compared to other treatments. On the other hand the activity of $Cu\text{-}HPO_4$ did not change with increasing P application.

6.3.4 PRIMARY DISTRIBUTION OF Cu AND P SPECIES

Complete solution composition (including organics) is needed for an accurate estimation of the primary distribution of all the elements. While exclusion of organics and other ions in my experiment will not influence the percentage distribution of Cu-P complexes, these omissions will affect the values of the free ion activity of Cu and P. My data showed that less than 0.10 per cent of the solution Cu was complexed with P in all treatments at each time (Table 6.7). In the control treatment, 0.2 per cent of the solution Cu was complexed with OH^- at 20 days, but it decreased to less than 0.1 per cent in subsequent time trials. The primary distribution of Cu-P complexes was not affected by P sources and levels, and the addition of Cu.

A major part of the solution P was either primary orthophosphate ($H_2PO_4^-$ and HPO_4^{2-}) or complexed with Fe (Table 6.8). Complex formation of P with Al and Ca was less than seven per cent. In the control at 20 days, 94 per cent of the solution P was in primary and secondary orthophosphate form and 4.4 per cent was complexed with Ca

(Table 6.8). In P treatments, distribution of P complexes was dependant on the rate of application. At the lower rate, more P was complexed with Fe than with H, while at higher rate, more P was complexed with H. In Cu alone treatment, a higher proportion of P was complexed with Fe than with H.

6.3.5 SOLUBILITY CONTROLLING SOLIDS

The soil solution of all treatments were undersaturated with respect to tenorite (CuO), cupric ferrite ($CuFe_2O_4$), $Cu_3(PO_4)$. $2H_2O$ and $Cu_3(PO_4)_2$ at each time. Addition of P and/or Cu did not result in the formation of known solubility controlling solids of Cu (Fig. 6.5). If there are no solubility controlling solids of Cu formed when the organics are omitted, they are less likely to form, when the organics are included in the model, because the activity of free Cu would be further reduced by the Cu-organic complexes. The soil solution was supersaturated with respect to soil-Fe ($Fe(OH)_3$) and other Fe oxides like maghemite ($1/2Fe_2O_3$) and hematite ($1/2\ Fe_2O_3$) in all the treatments at each time (Fig. 6.6). The stability diagram for P minerals was drawn (Fig. 6.7) using pH vs -log a $H_2PO_4^-$ as this ion is the dominant form of P in the pH range from 3.5 to 6.5 (Lindsay, 1979). All treatments were supersaturated with respect to octacalcium phosphate ($Ca_4H(PO_4)_3 \, . \, 2.5H_2O$), brushite ($CaHPO_4 \, . \, 2H_2O$) and monetite ($CaHPO_4$) and undersaturated with respect to fluorapatite ($Ca_5(PO_4)_3F$) and NH_4-taranakite ($H_6(NH_4)_3Al_5(PO_4)_8 \, . \, 18H_2O$). In all the P treatments the soil solution was supersaturated with respect to strengite ($FePO_4 \, . \, 2H_2O$). The control and Cu alone treatments were undersaturated with respect to strengite at 20 days, but in the last three periods, the control treatment was supersaturated with respect to strengite. There was no difference between APP and DAP with respect to the formation of any of the above solubility controlling solids for Cu and P.

6.4 DISCUSSION

The decrease in pH with time may have resulted partly from the organic acids produced during incubation. The lower pH in the treated soils compared to the control at 20 days can be explained by the displacement of the H^+ by the introduced cations (Cu^{2+} and/or NH_4^+) and/or the nitrification of the introduced NH_4^+ from APP and DAP. Similar low pH values for the soil solutions have been reported for the Ae horizons of podzols (Manley et al., 1987).

The composition of the soil solution showed that only a minor part of the added and native Cu remained in solution. This indicates that sorption processes (includes adsorption and surface precipitation) are controlling the reactions of Cu in my experimental soil. Activities of Cu-P complexes (predicted from the model) are lower than the activity of $H_2PO_4^{2-}$ (0.50 - 20 μmol L^{-1}) and HPO_4^- (0.30 - 30 nmol L^{-1}). The higher activity of $Cu\text{-}H_2PO_4^+$ (0.08 - 2.0 nmol L^{-1}) than $Cu\text{-}HPO_4$ (1 - 10 pmol L^{-1}) can be attributed to the low pH where $H_2PO_4^-$ activity was higher than HPO_4^{2-}. These Cu complexes, with such low activities, may have no practical significance. Higher activity of Fe^{3+} and H^+ in solution is consistent with the formation of P complexes with these ions leaving little phosphate to complex with Cu. This suggests that the native and added P may not be directly affecting the solution Cu, but may be influencing its reaction with solid surfaces (Chapter 3 and 4). Simard et al., 1988 found that most of the added P was removed from solution by adsorption or by precipitation, even when added at 125-250 mg P kg $soil^{-1}$. The sorbed P may change the surface characteristics and affect the sorption of the subsequently added metals. Mortvedt and Osborn (1977) also reported that the total soluble micronutrient concentrations were not affected by P applications.

Less than 0.20 per cent of the solution Cu was complexed with OH^-, and this may be due to the low pH of the soil solution. These results are in agreement with McBride and Blasik, 1979; Cavallaro and McBride, 1980, and Ritchie and Jarvis, 1986.

Undersaturation of soil solution with respect to various Cu minerals indicates that either the solubility-controlling solids for Cu were not present or the failure of the solubility product approach. Brummer et al. (1983) reported that metal solubility in soils, with the possible exception of Fe and Mn, was not controlled by the solubility product of a pure solid phase. In my experiment, the main process controlling Cu reactions in soil was sorption, since the total solution concentration of added Cu was low. When sorption processes are dominant, solution concentration of ions will be too low for precipitation, because homogeneous nucleation and precipitation can not occur unless the solubility product has been sufficiently exceeded to form a crystal nucleus. In addition, the solubility product approach may fail when the formation of solid solutions with ill-defined stoichiometry and/or of organo-Cu-mineral complexes occurs (McBride, 1989). In my study, there was no precipitation of Cu-P minerals based on the activity values of Cu predicted using GEOCHEM, when the organics were omitted. If soluble organics had been included in the model, the activity of free Cu would have been decreased further and the possibility of precipitation of Cu-P solids would have been even less likely. Therefore the Cu-P solids were not limiting the soil solution Cu in my experiment. Further it was shown that the formation of solubility controlling solids for Cu and P was not influenced by the form of added P.

6.5 SUMMARY AND CONCLUSIONS

Concentration of native and added Cu in the soil solution was low. Formation of Cu-P complexes in solution was not influenced by the addition of APP and DAP. $H_2PO_4^-$ is the dominant phosphate in soil solution, even though the form of P in DAP is HPO_4^{2-}. Solubility-controlling solids for Cu [tenorite, cupric ferrite, $Cu_3(PO_4) \cdot 2H_2O$ and $Cu_3(PO_4)_2$] were not present, and this supports the hypothesis that the sorption processes controlled the solution concentration of Cu (Chapter 3 and 4). Some of the Fe and Ca minerals were present as potential sinks for native and added P in this soil. However, there was no difference between APP and DAP with respect to the formation of solubility controlling solids for Cu and P.

Table 6.1 Soil solution composition as influenced by P sources and Cu at 20 days

Treaments	Zn 10^{-07}	Mn 10^{-06}	Fe 10^{-05}	Mg 10^{-04}	Ca 10^{-03}	Cu 10^{-07}	Al 10^{-05}	K 10^{-03}	NH_4 10^{-05}	NO_3 10^{-03}	PO_4 10^{-05}	SO_4 10^{-04}
	----------	----------	----------	----------	----------	----------	----------	mol L^{-1}	----------	----------	----------	----------
Control	3.68	0.18	5.61	7.15	2.42	2.62	2.96	1.61	1.15	1.40	0.58	1.35
	†(0.52)	(0.00)	(0.06)	(0.35)	(0.02)	(0.05)	(0.56)	(0.05)	(0.18)	(0.06)	(0.01)	(0.02)
APP15	4.73	6.73	6.57	5.98	2.09	2.10	5.93	1.36	2.33	1.17	1.24	1.12
	(0.00)	(0.10)	(0.00)	(0.31)	(0.10)	(0.25)	(0.22)	(0.01)	(0.80)	(0.07)	(0.05)	(0.05)
APP15+Cu	4.73	5.64	2.01	5.35	1.63	3.15	7.80	1.21	1.94	0.90	1.49	1.46
	(0.00)	(0.11)	(0.02)	(1.63)	(0.03)	(0.00)	(0.56)	(0.05)	(0.11)	(0.02)	(0.09)	(0.12)
APP30	4.73	8.13	4.77	7.13	2.53	2.10	7.80	1.48	1.43	1.40	2.14	1.19
	(0.00)	(0.77)	(0.15)	(1.57)	(0.20)	(0.05)	(0.37)	(0.02)	(0.11)	(0.18)	(0.14)	(0.06)
APP30+Cu	4.73	8.19	3.94	8.09	3.11	2.09	7.80	1.57	1.39	1.68	2.25	1.89
	(0.00)	(0.65)	(0.04)	(0.67)	(0.02)	(0.38)	(0.69)	(0.04)	(0.06)	(0.00)	(0.09)	(0.12)
DAP15	3.16	5.58	7.94	5.68	2.00	1.57	7.41	1.35	1.74	1.11	1.32	0.98
	(0.00)	(0.30)	(0.68)	(0.34)	(0.12)	(0.00)	(0.02)	(0.00)	(0.15)	(0.05)	(0.64)	(0.06)
DAP15+Cu	3.16	5.76	5.73	6.44	2.13	2.62	7.05	1.48	1.59	1.18	1.29	1.54
	(0.00)	(0.17)	(1.08)	(0.44)	(0.06)	(0.45)	(0.12)	(0.02)	(0.10)	(0.27)	(0.03)	(0.07)
DAP30	4.21	8.56	4.42	7.77	2.76	2.62	7.05	1.55	1.48	1.68	2.25	1.06
	(0.05)	(0.69)	(1.17)	(1.61)	(0.22)	(0.05)	(0.59)	(0.05)	(0.06)	(0.06)	(0.99)	(0.06)
DAP30+Cu	4.73	8.98	3.58	8.39	3.00	2.62	7.05	1.57	1.50	1.66	2.22	1.67
	(0.00)	(0.10)	(0.03)	(1.38)	(0.14)	(0.00)	(0.22)	(0.03)	(0.03)	(0.08)	(0.03)	(0.12)
Cu alone	3.68	4.37	7.40	5.94	2.08	3.15	5.95	1.34	1.63	1.14	0.61	1.58
	(0.05)	(0.11)	(0.07)	(0.24)	(0.09)	(0.05)	(0.22)	(0.16)	(0.07)	(0.05)	(0.00)	(0.04)

† Standard error of means (n=3)

Table 6.2 Soil solution composition as influenced by P sources and Cu at 40 days

Treaments	Zn 10^{-07}	Mn 10^{-06}	Fe 10^{-05}	Mg 10^{-04}	Ca 10^{-03}	Cu 10^{-07}	Al 10^{-03}	K 10^{-05}	NH_4 10^{-05}	NO_3 10^{-03}	PO_4 10^{-05}	SO_4 10^{-04}
	-------	-------	-------	-------	-------	-------	mol L^{-1}	-------	-------	-------	-------	-------
Control	5.26	0.97	3.70	0.86	3.02	2.10	8.15	1.70	0.89	1.54	0.73	1.35
	†(0.53)	(0.02)	(0.00)	(0.03)	(0.09)	(0.02)	(0.48)	(0.11)	(0.10)	(0.11)	(0.01)	(0.12)
APP15	5.79	1.26	4.77	0.91	3.24	2.10	7.05	1.75	1.07	1.54	1.40	1.38
	(0.11)	(0.03)	(0.85)	(0.02)	(0.18)	(0.05)	(0.54)	(0.23)	(0.20)	(0.03)	(0.03)	(0.03)
APP15+Cu	6.31	1.20	6.51	0.89	3.17	3.15	8.53	1.75	1.28	1.76	1.65	2.05
	(0.00)	(0.02)	(1.02)	(0.04)	(0.16)	(0.00)	(0.32)	(0.06)	(0.03)	(0.03)	(0.24)	(0.02)
APP30	5.79	1.53	3.52	0.97	3.51	1.57	8.89	1.75	1.28	1.73	2.15	1.46
	(0.05)	(0.08)	(0.52)	(0.01)	(0.04)	(0.00)	(0.55)	(0.05)	(0.03)	(0.02)	(0.02)	(0.02)
APP30+Cu	6.31	1.74	2.63	1.15	4.18	3.15	7.78	1.83	0.94	2.20	2.15	2.21
	(0.00)	(0.06)	(0.00)	(0.05)	(0.99)	(0.00)	(0.63)	(0.02)	(0.05)	(0.07)	(0.03)	(0.08)
DAP15	5.26	1.18	4.30	1.02	3.66	1.57	8.53	2.17	1.24	1.76	1.31	1.41
	(0.05)	(0.02)	(0.11)	(0.04)	(0.12)	(0.00)	(0.33)	(0.12)	(0.22)	(0.06)	(0.00)	(0.03)
DAP15+Cu	5.79	1.45	2.69	1.19	4.29	3.15	7.78	2.04	1.06	2.27	1.20	2.10
	(0.00)	(0.17)	(0.02)	(0.10)	(0.39)	(0.00)	(0.12)	(0.03)	(0.05)	(0.06)	(0.02)	(0.12)
DAP30	6.31	1.57	2.86	1.07	3.89	1.57	8.89	2.04	0.96	1.96	1.99	1.35
	(0.00)	(0.03)	(0.21)	(0.09)	(0.03)	(0.00)	(0.26)	(0.06)	(0.02)	(0.05)	(0.03)	(0.02)
DAP30+Cu	6.31	2.18	2.27	1.30	4.75	3.15	9.27	2.02	0.80	2.31	1.99	2.08
	(0.00)	(0.05)	(0.22)	(0.03)	(1.10)	(0.00)	(0.98)	(0.07)	(0.05)	(0.09)	(0.01)	(0.05)
Cu alone	4.73	0.84	4.30	0.87	3.12	3.15	7.78	2.01	7.96	1.57	0.67	1.93
	(0.52)	(0.06)	(0.76)	(0.07)	(0.25)	(0.00)	(0.06)	(0.03)	(0.07)	(0.16)	(0.04)	(0.10)

† Standard error of means (n=3)

Table 6.3 Soil solution composition as influenced by P sources and Cu at 60 days

Treaments	Zn 10^{-07}	Mn 10^{-06}	Fe 10^{-05}	Mg 10^{-04}	Ca 10^{-03}	Cu 10^{-07}	Al 10^{-05}	K 10^{-03}	NH_4 10^{-05}	NO_3 10^{-03}	PO_4 10^{-05}	SO_4 10^{-04}
	mol L^{-1}											
Control	5.26	0.87	1.59	0.94	3.41	2.10	7.41	1.58	3.61	1.86	1.22	1.38
	†(0.00)	(0.00)	(0.46)	(0.02)	(0.78)	(0.52)	(0.67)	(0.03)	(0.31)	(0.29)	(0.24)	(0.17)
APP15	5.26	1.51	1.40	1.22	4.53	2.10	8.53	1.79	4.02	2.41	1.81	1.52
	(0.52)	(0.22)	(0.24)	(0.44)	(0.16)	(0.00)	(0.27)	(0.04)	(0.41)	(0.32)	(0.12)	(0.02)
APP15+Cu	7.89	1.63	1.84	1.28	4.77	3.15	8.53	1.85	3.46	2.47	2.49	1.66
	(0.00)	(0.83)	(0.26)	(0.13)	(1.45)	(0.00)	(0.46)	(0.06)	(0.15)	(0.56)	(0.09)	(0.02)
APP30	7.89	1.78	1.31	1.25	4.72	1.57	8.89	1.78	3.46	2.47	2.49	1.66
	(0.53)	(0.63)	(0.60)	(0.52)	(0.19)	(0.00)	(0.97)	(0.00)	(0.19)	(0.65)	(0.07)	(0.31)
APP30+Cu	7.89	2.12	9.61	1.38	5.27	3.15	8.53	1.73	2.35	2.66	2.52	2.23
	(0.53)	(0.22)	(0.10)	(0.35)	(0.12)	(0.34)	(0.87)	(0.08)	(0.55)	(0.65)	(0.02)	(0.12)
DAP15	7.89	1.40	1.96	1.12	4.19	1.57	9.27	1.85	3.00	2.15	1.78	1.46
	(0.00)	(0.18)	(0.22)	(0.11)	(1.39)	(0.63)	(0.67)	(0.35)	(0.19)	(0.58)	(0.33)	(0.15)
DAP15+Cu	6.31	1.38	1.49	1.14	4.28	3.15	8.15	1.91	2.78	2.28	1.77	1.88
	(0.00)	(0.38)	(0.10)	(0.09)	(0.35)	(0.91)	(0.87)	(0.02)	(0.49)	(0.98)	(0.12)	(0.49)
DAP	6.84	2.09	1.40	1.29	4.95	1.57	8.53	1.83	2.59	2.59	2.50	1.49
	(0.00)	(0.47)	(0.16)	(0.27)	(0.11)	(0.80)	(0.56)	(0.00)	(0.67)	(0.16)	(0.37)	(0.96)
DAP30+Cu	7.89	2.52	7.10	1.50	5.81	3.15	7.78	2.28	2.30	2.87	2.43	2.05
	(0.53)	(0.63)	(0.63)	(0.70)	(0.96)	(0.00)	(0.01)	(0.00)	(0.31)	(0.44)	(0.09)	(0.20)
Cu alone	6.84	0.84	2.66	0.95	3.51	3.15	8.53	1.58	4.50	1.82	1.26	1.85
	(0.53)	(0.03)	(0.67)	(0.03)	(0.91)	(0.00)	(0.93)	(0.00)	(0.41)	(0.18)	(0.06)	(0.08)

† Standard error of means (n=3)

Table 6.4 Soil solution composition as influenced by P sources and Cu at 80 days

Treaments	Zn 10^{-07}	Mn 10^{-06}	Fe 10^{-05}	Mg 10^{-04}	Ca 10^{-03}	Cu 10^{-07}	NH_4 10^{-05}	NO_3 10^{-03}	PO_4 10^{-05}	SO_4 10^{-04}
	------------	------------	------------	------------	------------	------------	mol L^{-1}	------------	------------	------------
Control	6.31	1.04	1.91	1.26	4.48	1.57	1.70	2.87	0.98	1.59
	†(0.00)	(0.05)	(0.07)	(0.53)	(0.21)	(0.05)	(0.16)	(1.15)	(0.09)	(0.44)
APP15	4.73	1.26	1.91	1.18	4.28	1.57	1.54	2.69	1.56	1.52
	(0.00)	(0.07)	(0.00)	(0.30)	(0.10)	(0.00)	(0.28)	(0.03)	(0.07)	(0.55)
APP15+Cu	7.36	1.41	2.63	1.30	4.73	1.57	1.67	2.92	1.59	2.13
	(0.05)	(0.13)	(0.02)	(0.07)	(0.03)	(0.00)	(0.31)	(1.30)	(0.05)	(0.05)
APP30	7.36	1.74	2.33	1.42	5.20	1.57	2.59	3.28	2.16	1.74
	(0.05)	(0.08)	(0.01)	(0.01)	(1.05)	(0.00)	(0.21)	(0.02)	(0.04)	(0.07)
APP30+Cu	6.31	2.02	1.97	1.30	4.74	3.15	2.63	2.97	2.37	1.99
	(0.00)	(0.000	(0.21)	(0.01)	(0.48)	(0.00)	(0.18)	(0.05)	(0.03)	(0.02)
DAP15	6.31	1.48	2.39	1.20	4.36	1.57	1.61	2.81	1.50	1.68
	(0.92)	(0.24)	(0.32)	(0.01)	(0.05)	(0.00)	(0.58)	(0.06)	(0.04)	(0.18)
DAP15+Cu	6.31	1.37	1.73	1.29	4.68	2.62	0.83	2.97	1.45	1.87
	(0.00)	(0.07)	(0.02)	(0.02)	(0.03)	(0.05)	(0.08)	(0.05)	(0.03)	(0.04)
DAP30	5.79	2.34	2.27	1.488	5.42	1.57	1.04	3.48	2.08	1.58
	(0.55)	(0.21)	(0.02)	(0.09)	(0.03)	(0.00)	(0.15)	(0.19)	(0.04)	(0.06)
DAP30+Cu	6.31	2.03	2.21	1.26	4.64	3.15	1.07	2.96	2.17	1.80
	(0.00)	(0.01)	(0.00)	(0.05)	(0.02)	(0.00)	(0.04)	(0.11)	(0.04)	(0.05)
Cu alone	6.31	0.98	2.10	1.18	4.28	3.15	0.89	2.70	0.91	1.89
	(0.00)	(0.00)	(0.08)	(0.02)	(1.08)	(0.90)	(0.11)	(0.05)	(0.04)	(0.02)

† Standard error of means (n=3)

Table 6.5 Influence of P sources on the free ion activity of Cu, HPO_4^{2-} and $H_2PO_4^-$ (from GEOCHEM) in soil solution at different times of incubation

Treatments	Free Cu†				HPO_4^{2-}				$H_2PO_4^-$			
	days after incubation				days after incubation				days after incubation			
	20	40	60	80	20	40	60	80	20	40	60	80
	-log activity (mol L^{-1})				-log activity (mol L^{-1})				-log activity (mol L^{-1})			
Control	6.8	6.9	6.7	7.1	7.5	8.3	8.4	8.3	5.3	5.3	5.3	5.2
APP15	6.9	6.9	6.9	7.1	7.5	8.0	8.2	8.1	5.1	5.1	5.1	4.9
APP15+Cu	6.7	6.7	6.7	7.1	7.7	7.9	8.3	8.1	5.2	5.0	5.2	4.9
APP30	6.9	7.0	6.6	7.1	7.4	7.8	8.1	7.9	4.8	4.8	4.9	4.8
APP30+Cu	6.9	6.7	6.6	6.8	7.7	7.9	8.1	7.9	4.8	4.8	4.9	4.8
DAP15	6.9	7.0	6.6	7.1	7.9	8.1	8.4	8.2	5.1	5.1	5.2	4.9
DAP15+Cu	6.8	6.7	6.6	6.8	7.9	8.2	8.4	8.2	5.1	5.1	5.2	4.9
DAP30	6.8	7.0	6.6	7.1	7.6	7.9	8.2	8.1	4.8	4.9	4.9	4.8
DAP30+Cu	6.8	6.8	6.5	6.8	7.6	7.9	8.1	8.0	4.8	4.9	4.8	4.8
Cu	6.7	6.7	6.5	6.8	8.0	8.4	8.6	9.5	5.4	5.4	5.5	6.3

† includes ionic Cu and complexes of Cu with other unaccounted anions including organics

Table 6.6 Influence of P sources on the activity of the copper-phosphate complexes in soil solution at different times of incubation

Treatments	$Cu\text{-}H_2PO_4^+$				$Cu\text{-}HPO_4$			
	days after incubation				days after incubation			
	20	40	60	80	20	40	60	80
	-log activity (mol L^{-1})				-log activity (mol L^{-1})			
Control	10.6	10.6	10.5	10.7	11.0	12.0	11.9	12.1
APP15	10.4	10.4	10.5	10.4	10.1	11.3	11.7	11.9
APP15+Cu	10.3	10.2	10.3	10.5	11.2	11.4	11.7	11.9
APP30	10.2	10.3	9.9	10.3	11.2	11.6	11.5	11.8
APP30+Cu	10.2	10.0	9.9	9.9	11.3	11.4	11.5	11.4
DAP15	10.5	10.6	10.3	12.0	12.6	11.9	11.8	10.5
DAP15+Cu	10.3	10.3	10.2	10.3	11.4	11.7	11.7	11.8
DAP30	10.1	10.3	9.9	10.4	11.2	11.7	11.5	11.9
DAP30+Cu	10.1	10.1	9.8	10.0	11.2	11.5	11.3	11.5
Cu	10.6	10.6	10.5	11.5	11.6	11.9	11.9	12.9

Table 6.7 Influence of P sources on the percentage distribution of free and complexed Cu in soil solution at different times of incubation

Treatments	Free Cu†				Complexed with P				Complexed with OH$^-$			
	days after incubation				days after incubation				days after incubation			
	20	40	60	80	20	40	60	80	20	40	60	80
	%				%				%			
Control	98	99	99	99	0.02	0.00	0.00	0.01	0.18	0.02	0.02	0.01
APP15	99	99	99	99	0.01	0.02	0.00	0.03	0.06	0.02	0.02	0.01
APP15+Cu	98	98	98	98	0.00	0.02	0.00	0.02	0.06	0.02	0.02	0.01
APP30	99	99	99	99	0.04	0.02	0.02	0.03	0.04	0.02	0.02	0.01
APP30+Cu	98	98	98	98	0.04	0.04	0.03	0.04	0.03	0.02	0.01	0.02
DAP15	99	99	92	99	0.01	0.04	0.00	0.02	0.04	0.02	0.01	0.01
DAP15+Cu	94	98	98	98	0.02	0.02	0.00	0.02	0.04	0.02	0.01	0.01
DAP30	99	99	99	99	0.04	0.03	0.02	0.03	0.03	0.02	0.01	0.01
DAP30+Cu	98	98	98	98	0.04	0.03	0.03	0.04	0.03	0.02	0.01	0.01
Cu	98	98	98	98	0.00	0.00	0.00	0.00	0.04	0.02	0.02	0.01

† includes ionic Cu and complexes of Cu with other unaccounted anions including organics

Table 6.8 Influence of P sources on the percentage distribution of phosphate complexes in soil solution at different times of incubation

Treatments	Complexed with H†				Complexed with Fe				Complexed with Al		Complexed with Ca	
	days after incubation				days after incubation				days after incubation			
	20	40	60	80	20	40	60	80	20	60	20	60
	%				%				%			
Control	94	46	5.0	76	0.12	48	93	18	1.5	0.3	4.4	0.3
APP15	41	60	21	82	52	33	77	11	5.0	1.0	1.7	1.5
APP15+Cu	14	54	4.0	78	84	39	95	16	1.8	0.2	0.5	0.3
APP30	68	74	43	83	22	16	52	10	6.6	1.9	3.2	3.2
APP30+Cu	73	79	56	86	17	12	38	8.0	5.5	1.9	4.0	4.6
DAP15	35	60	3.0	79	59	32	96	15	3.7	0.1	1.4	0.2
DAP15+Cu	50	70	15	82	44	21	83	11	3.9	0.6	1.9	1.0
DAP30	72	76	40	83	19	14	55	10	5.3	1.5	3.5	3.1
DAP30+Cu	75	79	63	84	16	11	29	10	5.1	2.0	3.9	5.6
Cu	24	35	5.0	6.0	73	60	94	93	2.1	0.3	0.9	0.3

† includes HPO_4^{2-}, $H_2PO_4^-$ and H_3PO_4

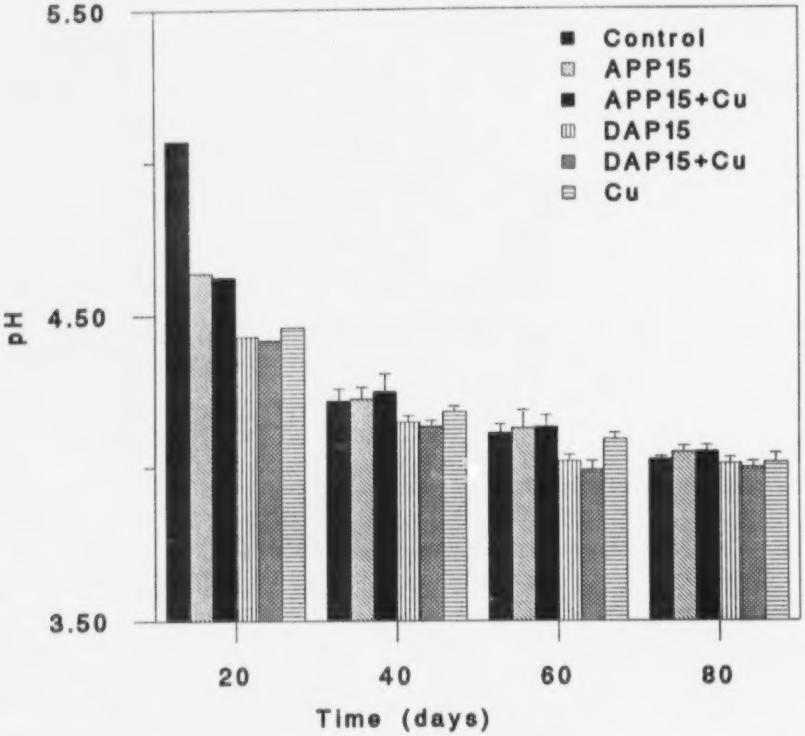


Fig. 6.1 Influence of P sources (at 15 μg P g soil^{-1}) and Cu on the pH of the saturated soil solution at different times (LSD values for comparing treatments at four times of sampling are 0.09, 0.09, 0.07 and 0.08 respectively)

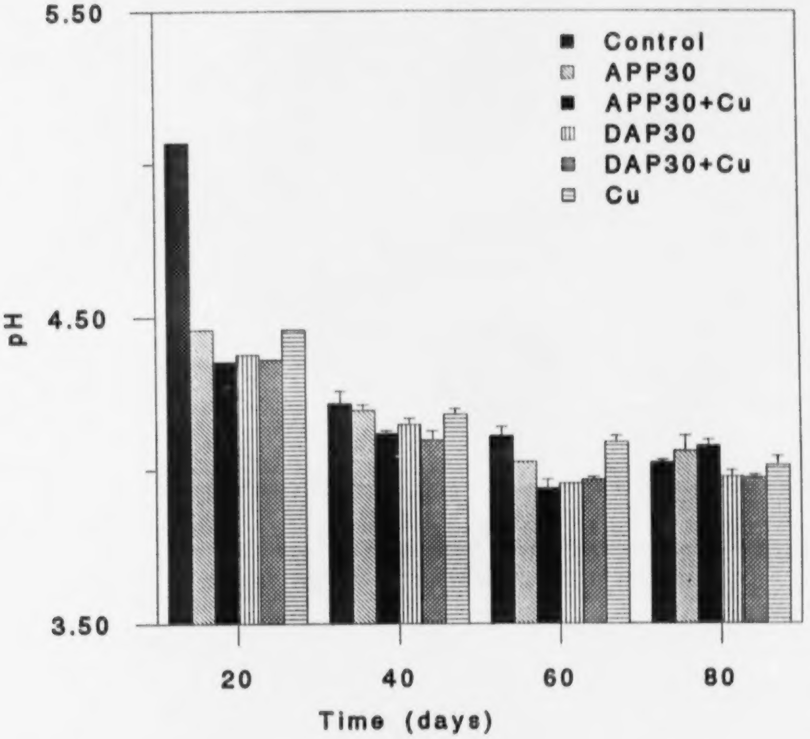


Fig. 6.2 Influence of P sources (at 30 μg P g soil^{-1}) and Cu on the pH of the saturated soil solution at different times (LSD values for comparing treatments at four times of sampling are 0.09, 0.09, 0.07 and 0.08 respectively)

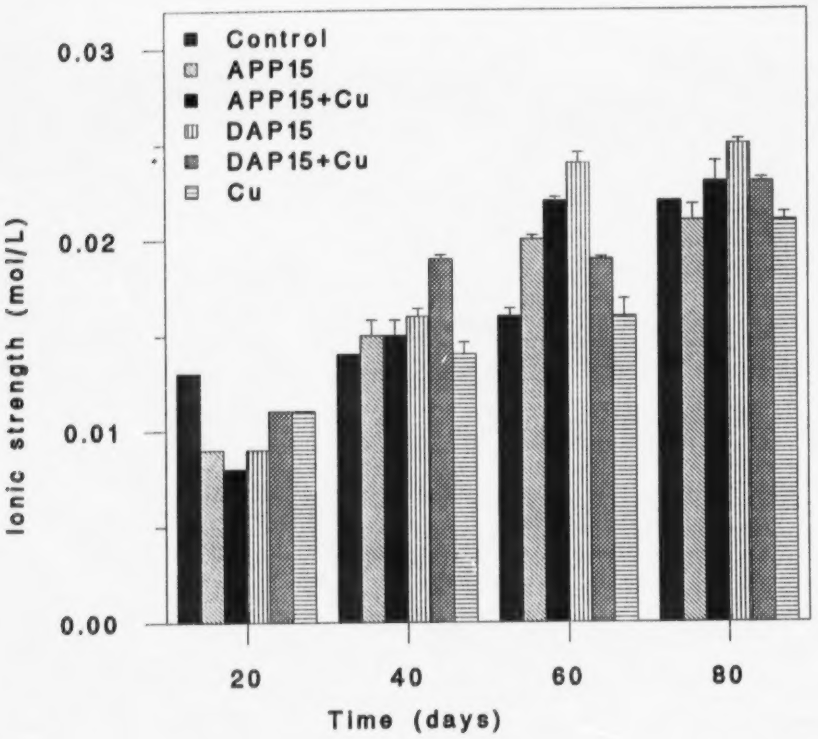


Fig. 6.3 Influence of P sources (at 15 μg P g soil^{-1}) and Cu on the ionic strength of the saturated soil solution at different times (LSD values for comparing treatments at four times of sampling are 0.002, 0.002, 0.003 and 0.005 respectively)

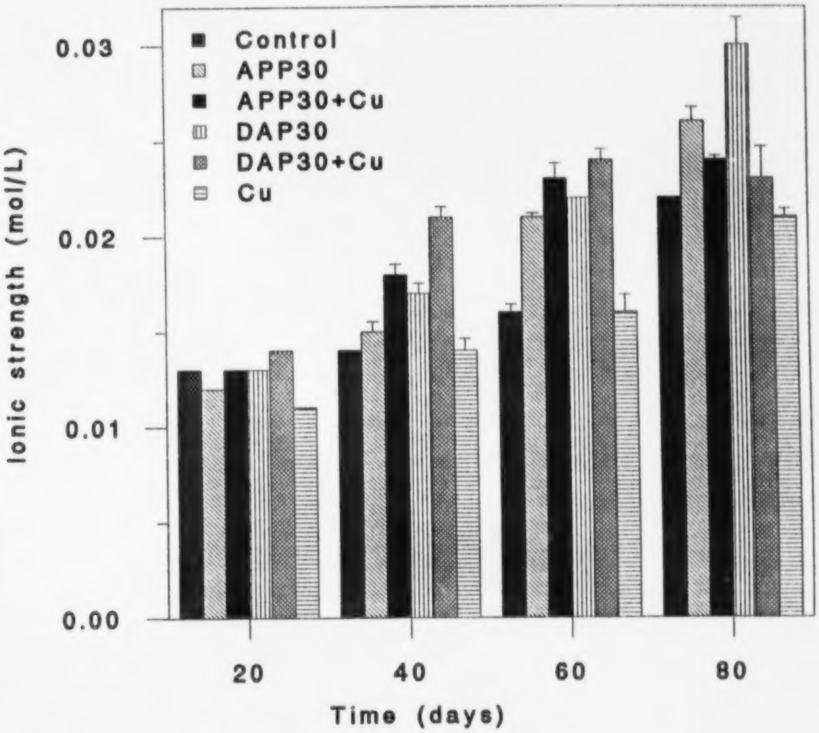


Fig. 6.4 Influence of P sources (at 30 μg P g soil^{-1}) and Cu on the ionic strength of the saturated soil solution at different times (LSD values for comparing treatments at four times of sampling are 0.002, 0.002, 0.003 and 0.005 respectively)

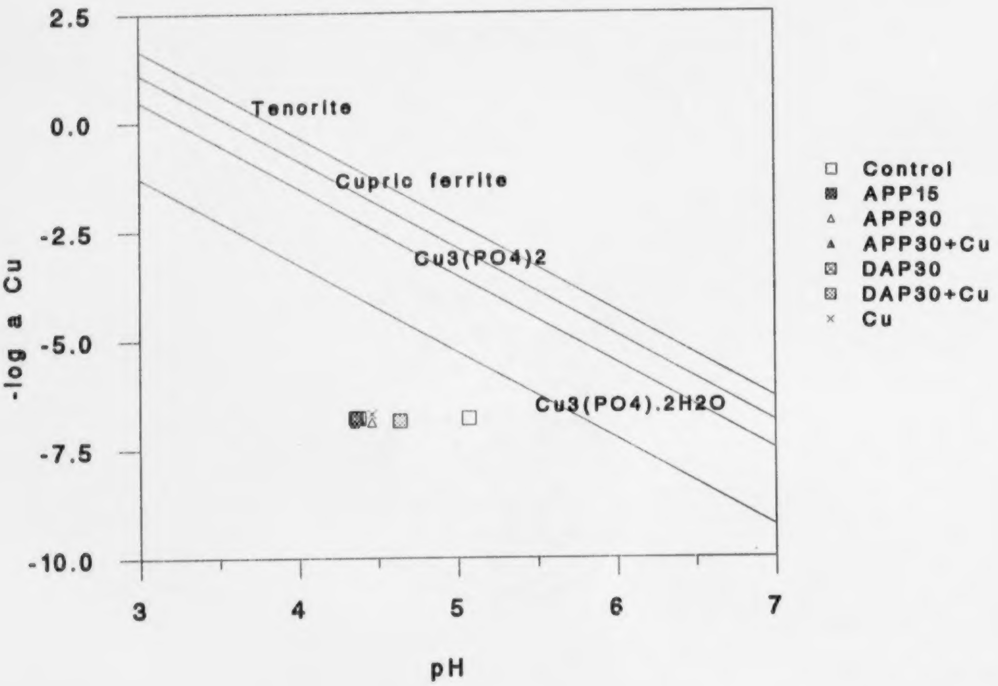


Fig. 6.5 Solubility equilibria of some Cu minerals and activity of Cu in saturated soil solution from various treatments (data from 20 days incubation)

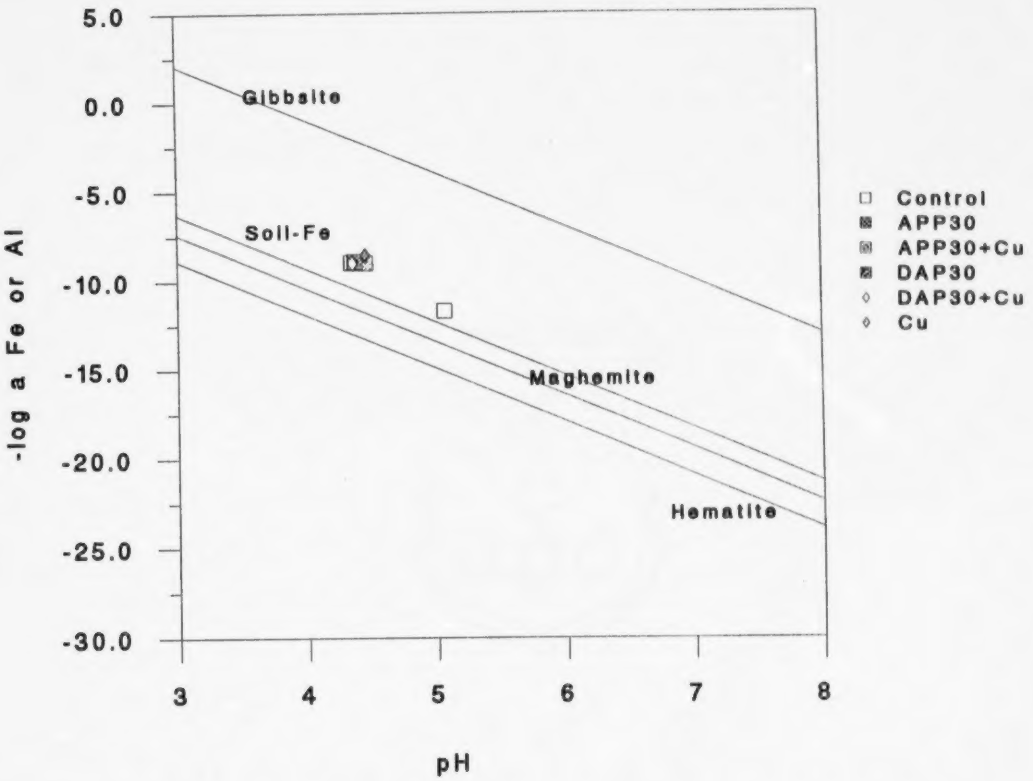


Fig. 6.6 Solubility equilibria of some Fe and Al minerals and activity of Fe and Al in saturated soil solution from various treatments (data from 20 days incubation)

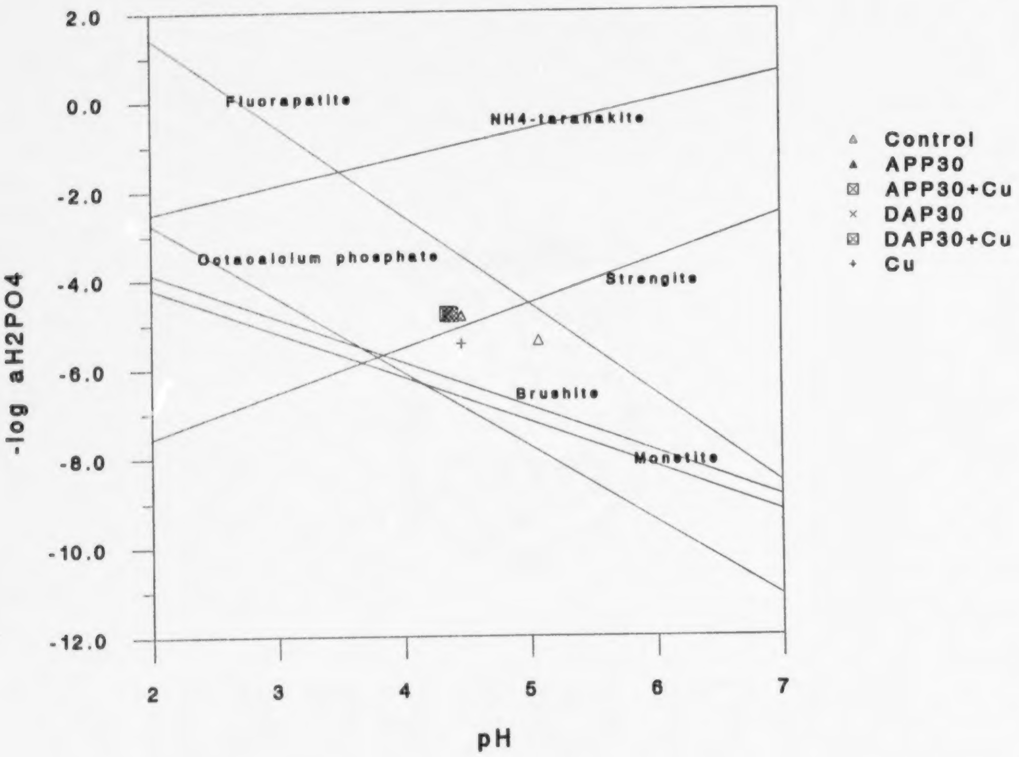


Fig. 6.7 Solubility equilibria of some phosphate minerals and activity of H_2PO_4 in saturated soil solution from various treatments (data from 20 days incubation)

6.6 REFERENCES

Brummer, G., K.G. Tiller, U. Herms, and P.M. Clayton. 1983. Adsorption-desorption and/or precipitation-dissolution processes of Zn in soils. Geoderma. 31: 337-354.

Cavallaro, N., and M.B. McBride. 1980. Activities of Cu^{2+} and Cd^{2+} in soil solution as affected by pH. Soil Sci. Soc. Am. J. 44: 729-732.

Griffin, R.A., and J. J. Jurinak. 1973. Estimation of activity coefficients from the electrical conductivity of natural aquatic systems and soil extracts. Soil Sci. 116: 26-30.

Leckie, J. O., and J. A. Davis. 1979. Aqueous environmental chemistry of Cu p 90-121. *In* Nriagu, J. O. (ed.) Cu in the Environment. Part 1: Ecological cycling. Wiley-Interscience, New York.

Lindsay, W.L. 1979. Chemical equilibria in soils. John Wiley and Sons, New York.

Manley, E. P., W. Chesworth, and L. J. Evans. 1987. The solution chemistry of podzolic soils from the eastern Canadian shield: a thermodynamic interpretation of the mineral phases controlling soluble Al^{3+} and H_2SiO_4. J. Soil Sci. 38: 39-51.

McBride, M.B. 1989. Reactions controlling heavy metal solubility in soils. p 1-47. *In* Stewart, B.A. (ed.) Advances in Soil Sci. Springer-Verlag.

McBride, M. B., and J.J. Blasik. 1979. Zinc and copper solubility as a function of pH in an acid soil. Soil Sci. Soc. Am. J. 43: 866-870.

Mortvedt, J. J. and G. Osborn. 1977. Micronutrient concentrations in soil solution after ammonium phosphate application. Soil Sci. Soc. Am. J. 41:1004-1009.

Parker, D.R., W.A. Norvell, and R.L. Chaney. 1990. GEOCHEM-PC, Version 2.0 Univ. of California, Riverside.

Ritchie, G.S.P., and S.C. Jarvis. 1986. Effect of inorganic speciation on the interpretation of Cu adsorption by soils. J. Soil Sci. 37: 205-210.

Sanders, J. R. 1982. The effect of pH upon the copper and cupric ion concentrations in soil solutions. J. Soil Sci. 33: 679-689.

SAS Institute Inc. 1987. SAS/STAT guide for personal computers. Version 6 Edition, Cary, N. C: SAS Institute Inc.

Simard, R. R., L. J. Evans, and T. E. Bates. 1988. The effects of additions of $CaCO_3$ and P on the soil solution chemistry of a podzolic soil. Can. J. Soil Sci. 68: 41-52.

Sposito, G., and S. V. Mattigod. 1979. GEOCHEM: a computer program for the calculation of chemical equilibria in soil solution and other natural systems. Dept. of Soil and Environ. Sci. Univ. of California

Chapter 7

GENERAL DISCUSSION AND CONCLUSIONS

Copper deficiency is the most prevalent micronutrient problem of cereal grain production in Alberta. One of the causes of low availability of Cu is its reaction with orthophosphates added in the conventional P fertilizers. Some of the condensed phosphates present in polyphosphatic fertilizers increase the concentration of soluble metals in solution (Lindsay et al., 1962; Bar-Yosef and Asher, 1982), and are more strongly sorbed on the soil (Sutton and Larsen, 1964; Xie and MacKenzie, 1990). Linear condensed phosphates have high rotational flexibility about the P-O-P linkages, and unlike many complexing ligands, linear polyphosphates are not specific to the coordination requirement of particular cations (Corbridge, 1985). This allows them to form complexes with most metallic cations. In addition, some of the condensed phosphates solubilize the soil organic matter (McKeague, 1967; Schnitzer and Schuppli, 1989), by complexing with bound metals, and thus increasing solubility. Those chemical properties of polyphosphates present in ammonium polyphosphate (APP) suggest that APP can be used for treating the soils deficient in micronutrients. However, there have not been any studies to show the effect of APP on the solubility and uptake of Cu from a Cu deficient soil. Therefore, a greenhouse and a series of incubation experiments were conducted, using a Cu deficient soil sample, with the objectives of finding the effect of polyphosphate and orthophosphate on the uptake of Cu by wheat, and of determining how those two forms influence the sorption-desorption reactions, and the inorganic speciation of Cu in soil solution in a Cu deficient soil.

The soil used in the experiments was a sandy loam with low pH (5.52) and CEC (12 cmol (+) kg soil^{-1}). The soil had been cultivated for an estimated 90 years, and no Cu fertilizers have been used. The total Cu content (5.4 μg Cu g soil^{-1}) was lower than the average crustal abundance of 55 μg Cu g soil^{-1} (Krauskopf, 1967). The DTPA extractable Cu (0.35 μg Cu g soil^{-1}) was below the critical value (0.60 μg Cu g soil^{-1}) established for the Cu deficiency in Alberta.

In the greenhouse experiment, visual symptoms of Cu deficiency occurred at one month after sowing in treatments which did not receive Cu and/or APP. This may be the result of the higher sorption of added Cu and subsequent lower desorption, in the presence of DAP as compared to APP (Chapter 3 and 4). Copper deficiency affected grain yield more than straw yield. Without added Cu, total Cu uptake was greater with the application of APP than with DAP. However, P uptake was higher in DAP treatments than in APP treatments. This might be due to the lower sorption of DAP than APP (Chapter 3). My findings of the increased Cu uptake in wheat by the APP application was parallel to the reports of Giordano and Mortvedt (1969); Mortvedt and Giordano (1969, 1975), and Hashimoto and Wakefield (1974) for Zn and Mn.

Sorption (including adsorption and surface precipitation) is the major process controlling the partitioning of solutes between soil solids and solution at low added concentration. The amount of added solute going to the solid depends on the surface characteristics of the adsorbents. Since the linear polyphosphates and orthophosphates have different structures, their orientation on the surfaces may influence the sorption of Cu. Consequently, incubation experiments were conducted to assess the influence of added APP and DAP on the sorption of Cu including their sorption kinetics (Cu and P).

Concentration of P will be high near the fertilizer granule at least soon after its application. This immediate effect of added P on the sorption of Cu (Chapter 3) showed that the form of added P influenced the Cu sorption. Increased sorption of APP as compared to DAP (Table 3.1) might have decreased the sorption of Cu by blocking the high affinity sites. This could cause a greater desorption of sorbed Cu from APP pretreated soil than from soils pretreated with DAP (Table 3.1). The low sorption of Cu with APP pretreatment is advantageous for plant uptake of Cu. Sutton and Larsen (1964), Blanchar and Hossner (1969), and Xie and MacKenzie (1990) also reported a higher sorption of polyphosphates than orthophosphates. The higher sorption of added APP as compared to DAP, may partly contribute to the lower uptake of P by wheat in the greenhouse experiment (Chapter 2).

In addition to the short-term influence of P sorption on Cu (Chapter 3), reactions of Cu with time after the addition of the P sources are important to assess the solubility of Cu in soil and its availability to plants (Chapter 4). In soil, diffusion of solutes to the interior of microaggregates with time is suggested by Barrow (1983). This diffusion may change the surface characteristics of soil solids with time after the addition of P, and consequently, the sorption of Cu can change. Low concentrations of P (15 and 30 μg P g $soil^{-1}$) and Cu (0 to 10 μg Cu g $soil^{-1}$) were used (Chapter 4) to simulate the soil conditions where the fertilizers were mixed throughout the soil as in the greenhouse experiment (Chapter 2). Copper sorption was higher when DAP was applied at 30 μg P g $soil^{-1}$ as compared to APP. Regardless of P sources, Cu sorption decreased with time up to 60 days after the P pretreatment. A higher Kd for Cu sorption was found when the soil was pretreated with DAP than with APP (Chapter 3 and 4). This might contribute to the higher plant absorption of Cu with APP addition than with DAP.

Kinetics of P and Cu depletion from the solution (Chapter 5) showed that a major part of the added P and Cu was sorbed in the first 15 min. after their addition. The high activation energy (Ea) and activation enthalpy, and less negative activation entropy values of Cu depletion, with APP than with DAP could cause a greater Cu sorption in DAP pretreated soil than in APP pretreated soil. This may result in a lower desorption of Cu and subsequent lower Cu uptake by plants from DAP pretreated soil than APP pretreated soil. However, a higher rate constant, lower Ea and activation enthalpy, and more negative activation entropy values for APP depletion than for DAP might have caused a faster and greater sorption of APP than DAP by soil. The high rate of APP sorption may block a major part of the naturally occurring high affinity sorption sites for Cu sorption resulting in a lower partition coefficient of Cu in its presence than in the case of DAP.

The concentration of Cu in soil solution was very low when added with APP and DAP (Chapter 6). Inorganic speciation of Cu showed that the Cu-P complex formation is not affected by the form of added P.

7.1 PRACTICAL IMPLICATIONS

Results from my greenhouse and incubation experiments showed that the application of APP in a Cu deficient soil overcame the deficiency in wheat, and this finding may be applicable to the field. However, in my studies APP, DAP and Cu were applied in solution and mixed with soil, while, granules (including APP and Cu) would be used in farm conditions for correcting Cu deficiency. The metal complexing ability of polyphosphates at higher concentration would be an added advantage to keep Cu soluble near the APP fertilizer granule in the field for a substantial period. Diammonium phosphate increased the P uptake more than APP in my experiment, but, the Cu uptake by wheat was lower even when DAP was added with Cu as compared to APP. Apparently, APP is preferred to DAP for application in Cu deficient soil.

7.2 FUTURE RESEARCH

My experiments provided a general understanding of the reactions of APP and DAP with Cu on soil solids, and their influence on the growth and uptake of Cu by wheat. However, future research may be focussed to the following concepts. Determination of inorganic and organic speciation of Cu, when the soil moisture content is less than water saturation is important to understand the reactions of Cu in soil solution. Identification of specific sorbing sites (organic and inorganic) for Cu sorption will help in the proper management of Cu fertilizers. Since the granular form of fertilizers are more common, determination of the solubility of Cu with time when the fertilizer granule containing Cu and APP is added to the soil is important. The better performance of the APP than DAP with respect to Cu uptake in the greenhouse should be verified in the field at different Cu deficient locations and with other cereal grains.

7.3 REFERENCES

Bar-Yosef, B., and L. E. Asher. 1982. Reactions of pyrophosphate in soils and its effect on Zn sorption at various pH levels. Soil Sci. 136: 82-88.

Barrow, N. J. 1983. A mechanistic model for describing the sorption and desorption of phosphate by soil. J. Soil Sci. 34: 733-750.

Blanchar, R. W., and L. R. Hossner. 1969. Hydrolysis and sorption reactions of orthophosphate, pyrophosphate and tripolyphosphate anions added to an Elliot soil. Soil Sci. Soc. Am. Proc. 33: 141-144

Corbridge, D. E. C. 1985. Phosphorus: An outline of its chemistry, biochemistry and technology. 3rd ed. Elsevier Sci. Publishers, New York.

Giordano, P. M. and J. J. Mortvedt. 1969. Phosphorus availability to corn as affected by granulating Mn with ortho and pyrophosphate fertilizers. Proc. Soil Sci. Soc. Am. 33: 460-463.

Hashimoto I. and Z. T. Wakefield. 1974. Hydrolysis of pyrophosphate in soils: response to temperature and effect on heavy metal uptake by plants. Soil Sci. 118: 90-94.

Krauskopf, K. 1967. Introduction to geochemistry. McGraw-Hill, Inc. New York.

Lindsay, W.L., A.W. Frazier, and H. F. Stephenson. 1962. Identification of reaction products from P fertilizers in soils. Proc. Soil Sci. Soc. Am. 26: 446-452.

McKeague, J. A. 1967. An evaluation of 0.1 M pyrophosphate and pyrophosphate-dithionite in comparison with oxalate as extractants of the accumulation products in podzols and some other soils. Can. J. Soil Sci. 47: 96-99.

Mortvedt J. J. and Giordano, P. M. 1969. Availability to corn of Zn applied with various macronutrient fertilizers. Soil Sci. 108: 180-187.

Mortvedt J. J. and Giordano, P. M. 1975. Crop response to Mn sources applied with ortho and polyphosphate fertilizers. Proc. Soil Sci. Soc. Am. 39: 782-784.

Schnitzer, M., and P. Schuppli. 1989. The extraction of organic matter from selected soils and particle size fractions with 0.5 M NaOH and 0.1 M $Na_4P_2O_7$ solutions. Can. J. Soil Sci. 69: 253-262.

Sutton, C. D., and S. Larsen. 1964. Pyrophosphate as a source of P for plants. Soil Sci. 97: 196-201.

Xie, R. J., and A. F. MacKenzie. 1990. Sorbed ortho-and pyrophosphate effects on Zn reactions compared in three autoclaved soils. Soil Sci. Soc. Am. J. 54: 744-750.

Appendix 1 Chemical analysis of ammonium polyphosphate (APP)

Total P	16.64 %
Polyphosphate content	75 % of total P
N	11.1 %
Ca	1.6 μg Ca mL^{-1}
Mg	1.8 μg Mg mL^{-1}
Fe	2.4 μg Fe mL^{-1}
Al	2.0 μg Al mL^{-1}
Cu	BDL*
Zn	0.10 μg Zn mL^{-1}
Na	1.1 μg Na mL^{-1}
Cd	0.02 μg Cd mL^{-1}
Mn	0.03 μg Mn mL^{-1}
Mo	BDL
As	BDL
Pb	BDL
Hg	BDL
Se	BDL
Co	BDL

---

* Below detection limit

Appendix 2 Procedure used for the microwave digestion (HNO_3-H_2O_2) of wheat samples

Dried and ground plant samples (0.50 g) were treated with 5 mL of HNO_3 (in Teflon flasks) for 5 minutes. After the predigestion, the samples were digested in a microwave oven (CEM, Model MDS - 81) at 90 per cent (540 watts) power for 15 minutes. At the end of this period, 5 mL of H_2O_2 was added to each sample, and digestion continued for 10 more minutes. Samples were cooled after digestion and diluted to 50 mL with double distilled water, filtered, and used for the elemental analysis. Total concentrations of Cu, P and Zn were determined using Inductively Coupled Plasma Emission Spectroscopy (ICPES). Blanks, calibration standards and known wheat flour standards were used for quality control. Blank and the wheat flour standard were used for every 12 samples digested. Calibration standards were prepared from ICP-grade standard solutions and included in every 12 samples during ICPES determination of Cu, P and Zn in the wheat samples.

Appendix 3 Influence of P sources, Cu and Zn on the total dry matter yield at different times of sampling

Treatments	Total dry matter yield				
	20d	40d	60d	Maturity	Mean
	g plant^{-1}				
Control	0.07 (0.00)†	0.25 (0.08)	1.83 (0.34)	1.90 (0.10)	1.02
APP	0.12 (0.01)	0.51 (0.12)	1.86 (0.32)	2.25 (0.09)	1.19
APP+Zn	0.11 (0.03)	0.54 (0.08)	1.93 (0.26)	2.21 (0.41)	1.20
APP+Cu	0.12 (0.06)	0.56 (0.08)	2.07 (0.31)	2.54 (0.57)	1.33
DAP	0.10 (0.03)	0.40 (0.09)	1.79 (0.21)	1.98 (0.31)	1.07
DAP+Zn	0.11 (0.01)	0.35 (0.11)	1.86 (0.43)	2.13 (0.13)	1.11
DAP+Cu	0.11 (0.02)	0.53 (0.14)	2.11 (0.53)	2.46 (0.35)	1.30
Zn	0.07 (0.08)	0.38 (0.09)	1.78 (0.28)	2.06 (0.15)	1.07
Cu	0.08 (0.06)	0.44 (0.05)	1.81 (0.28)	2.27 (0.22)	1.16
LSD (0.05)	0.01	0.09	0.17	0.19	

ANOVA for the total yield of wheat

Sources	df	Sum of squares	Mean square	F	P>F
Treatment (Trt)	8	1.049	0.131	20.87	0.0001
Time	3	88.22	29.41	4677	0.0001
Trt x Time	24	0.617	0.026	4.09	0.0001
Error	72	0.453	0.006		
Total	107	90.34			

† Standard error of mean (n=3)

Appendix 4. ANOVA for the yield of grain and straw at harvest and grain:straw ratio

Sources	df	Sum of squares	Mean square	F	P>F
Total dry matter yield at maturity					
Treatment	8	1.053	0.132	10.95	0.0001
Error	18	0.216	0.012		
Total	26	1.270			
Yield of grain					
Treatment	8	0.863	0.108	15.94	0.0001
Error	18	0.122	0.007		
Total	26	0.985			
Yield of straw at maturity					
Treatment	8	0.103	0.013	2.11	0.089
Error	18	0.110	0.006		
Total	26	0.214			
Grain:Straw ratio					
Treatment	8	0.643	0.080	8.44	0.0001
Error	18	0.171	0.009		
Total	26	0.815			

Appendix 5 Influence of P sources, Cu and Zn on the concentration of Cu in shoot at different times of sampling

	Concentration of Cu at				
Treatments	20d	40d	60d	Maturity	Mean
			mg Cu kg^{-1}		
Control	2.60 (0.07)†	4.10 (0.34)	2.16 (0.17)	1.47 (0.11)	2.58
APP	2.67 (0.14)	5.20 (0.27)	2.60 (0.20)	1.61 (0.03)	3.02
APP+Zn	2.72 (0.13)	2.24 (0.17)	2.15 (0.10)	1.39 (0.09)	2.13
APP+Cu	7.03 (0.13)	8.04 (0.23)	3.94 (0.09)	3.23 (0.17)	5.56
DAP	2.76 (0.35)	2.41 (0.06)	2.20 (0.15)	1.15 (0.05)	2.13
DAP+Zn	2.60 (0.04)	2.34 (0.20)	2.28 (0.03)	1.48 (0.10)	2.18
DAP+Cu	6.37 (0.25)	4.49 (0.19)	4.20 (0.17)	2.18 (0.16)	4.31
Zn	5.13 (1.20)	2.37 (0.03)	3.35 (0.22)	2.08 (0.15)	3.23
Cu	9.96 (0.33)	4.15 (0.16)	3.70 (0.21)	4.98 (1.98)	5.20
LSD (0.05)	1.36	0.62	0.49	0.36	

ANOVA for the concentration of Cu in shoot

Sources	df	Sum of squares	Mean square	F	P>F
Treatment (Trt)	8	196.2	24.53	44.63	0.0001
Time	3	95.52	31.84	57.93	0.0001
Trt x Time	24	113.9	4.746	8.64	0.0001
Error	72	39.58	0.549		
Total	107	445.2			

†Standard error of mean (n=3)

Appendix 6 Influence of P sources, Cu and Zn on the total uptake of Cu by wheat at different times of sampling

Treatments	Total uptake of Cu				
	20d	40d	60d	Maturity	Mean
	μg Cu plant^{-1}				
Control	0.20 (0.00)†	1.06 (0.02)	3.96 (0.41)	3.01 (0.16)	2.06
APP	0.32 (0.04)	2.65 (0.13)	4.81 (0.41)	3.94 (0.25)	2.92
APP+Zn	0.29 (0.06)	1.22 (0.07)	4.16 (0.11)	3.36 (0.07)	2.26
APP+Cu	0.88 (0.07)	4.53 (0.02)	8.15 (0.58)	9.27 (0.11)	5.70
DAP	0.27 (0.04)	0.98 (0.15)	3.95 (0.22)	2.56 (0.13)	1.94
DAP+Zn	0.28 (0.00)	0.79 (0.26)	4.25 (0.57)	2.93 (0.29)	2.06
DAP+Cu	0.69 (0.01)	2.38 (0.08)	8.89 (0.23)	6.90 (0.19)	4.72
Zn	0.35 (0.02)	0.90 (0.08)	5.98 (0.34)	4.41 (0.02)	2.92
Cu	0.84 (0.03)	1.86 (0.01)	6.68 (0.08)	11.1 (0.19)	5.10
LSD (0.05)	0.14	0.30	1.01	2.19	

ANOVA for the total uptake of Cu by wheat

Sources	df	Sum of squares	Mean square	F	P>F
Treatment (Trt)	8	209.4	26.17	51.98	0.0001
Time	3	531.9	177.3	352.2	0.0001
Trt x Time	24	145.2	6.05	12.02	0.0001
Error	72	36.25	0.503		
Total	107	922.8			

† Standard error of mean (n=3)

Appendix 7 Influence of P sources, Cu and Zn on the concentration of P in shoots at different times of sampling

	Concentration of P				
Treatments	20d	40d	60d	Maturity	Mean
	g P kg^{-1}				
Control	3.84(0.15)†	2.46 (0.06)	1.73 (0.23)	0.42 (0.01)	2.11
APP	5.32 (0.36)	2.93 (0.26)	1.83 (0.29)	0.74 (0.17)	2.70
APP+Zn	5.38 (0.09)	3.08 (0.13)	1.45 (0.06)	0.67 (0.11)	2.65
APP+Cu	4.41 (0.23)	2.80 (0.04)	1.78 (0.27)	0.43 (0.05)	2.36
DAP	5.79 (0.16)	3.95 (0.11)	2.50 (0.14)	1.15 (0.17)	3.35
DAP+Zn	5.87 (0.07)	3.83 (0.02)	3.06 (0.21)	0.93 (0.10)	3.42
DAP+Cu	5.34 (0.31)	3.23 (0.04)	2.40 (0.12)	0.52 (0.06)	2.87
Zn	3.85 (0.11)	2.53 (0.04)	1.89 (0.19)	0.38 (0.04)	2.16
Cu	3.81 (0.11)	1.99 (0.95)	1.30 (0.10)	0.28 (0.00)	1.84
LSD (0.05)	0.62	0.34	0.59	0.30	

ANOVA for concentration of P in shoot

Sources	df	Sum of squares	Mean square	F	P>F
Treatment (Trt)	8	28.55	3.57	44.5	0.0001
Time	3	256.6	85.5	1066	0.0001
Trt x Time	24	8.405	0.35	4.37	0.0001
Error	72	5.773	0.08		
Total	107	299.3			

† Standard error of mean (n=3)

Appendix 8 Influence of P sources, Cu and Zn on the total uptake of P by wheat at different times of sampling

Treatments	Total uptake of P				
	20d	40d	60d	Maturity	Mean
	mg P $plant^{-1}$				
Control	0.30 (0.00)†	0.63 (0.00)	3.17 (0.02)	3.36 (0.07)	1.86
APP	0.64 (0.00)	1.49 (0.01)	3.34 (0.11)	4.59 (0.07)	2.52
APP+Zn	0.58 (0.01)	1.67 (0.00)	2.78 (0.06)	4.19 (0.03)	2.30
APP+Cu	0.55 (0.01)	1.58 (0.01)	3.68 (0.00)	4.43 (0.02)	2.56
DAP	0.57 (0.01)	1.59 (0.01)	4.48 (0.01)	5.64 (0.13)	3.08
DAP+Zn	0.64 (0.00)	1.32 (0.03)	5.73 (0.06)	5.39 (0.00)	3.28
DAP+Cu	0.58 (0.00)	1.71 (0.07)	5.08 (0.02)	5.48 (0.07)	3.22
Zn	0.27 (0.01)	0.96 (0.02)	3.36 (0.04)	3.40 (0.04)	2.00
Cu	0.32 (0.00)	0.89 (0.04)	2.34 (0.08)	3.85 (0.05)	1.97
LSD (0.05)	0.12	0.35	1.10	0.53	

ANOVA for the total uptake of P by wheat

Sources	df	Sum of squares	Mean square	F	P>F
Treatment (Trt)	8	30.50	3.812	27.37	0.0001
Time	3	296.2	98.74	708.9	0.0001
Trt x Time	24	21.37	0.890	6.39	0.0001
Error	72	10.03			
Total	107	358.1			

† Standard error of mean (n=3)

Appendix 9 Influence of P sources, Cu and Zn on the concentration of Zn in shoot at different times of sampling

Treatments	Concentration of Zn 20d	 40d	 60d	 Maturity	 Mean
	----------	----------	mg Zn kg^{-1}	----------	----------
Control	33.6 (1.13)†	35.0 (0.18)	27.6 (0.70)	19.8 (0.52)	29.0
APP	38.4 (2.02)	36.9 (4.68)	30.8 (1.41)	20.2 (0.86)	31.3
APP+Zn	53.2 (0.67)	52.7 (0.93)	42.8 (1.00)	39.9 (2.89)	47.2
APP+Cu	36.8 (1.27)	32.9 (1.38)	26.3 (1.91)	12.1 (0.89)	27.0
DAP	40.4 (1.49)	39.3 (2.91)	29.3 (2.82)	19.7 (2.04)	32.2
DAP+Zn	49.6 (0.62)	55.4 (1.35)	46.4 (1.46)	37.6 (2.19)	47.2
DAP+Cu	35.3 (1.45)	31.5 (1.50)	25.3 (0.65)	10.6 (0.17)	25.7
Zn	49.6 (2.60)	62.6 (5.66)	44.7 (1.40)	29.1 (1.77)	46.5
Cu	34.6 (2.30)	27.0 (0.95)	19.9 (1.91)	8.45 (0.37)	22.5
LSD (0.05)	4.9	15.7	4.8	4.7	

ANOVA for the concentration of Zn in shoot

Sources	df	Sum of squares	Mean square	F	P>F
Treatment (Trt)	8	9468	1183	44.45	0.0001
Time	3	6908	2302	86.49	0.0001
Trt x Time	24	856.8	35.70	1.34	0.1708
Error	72	1916	26.62		
Total	107	19150			

† Standard error of mean (n=3)

Appendix 10 Influence of P sources, Cu and Zn on the total uptake of Zn by wheat at different times of sampling

	Total uptake				
Treatments	20d	40d	60d	Maturity	Mean
	----------------------------------		μg Zn $plant^{-1}$	-------------------------	
Control	2.60(0.09)†	9.02 (0.00)	50.7 (1.47)	68.8 (0.71)	32.8
APP	4.60 (0.20)	18.8 (2.16)	57.2 (3.87)	79.8 (10.3)	40.1
APP+Zn	5.78 (0.54)	28.6 (0.59)	82.5 (0.93)	113 (4.92)	57.7
APP+Cu	4.61 (0.48)	18.5 (0.58)	54.3 (4.12)	69.0 (4.09)	36.6
DAP	3.96 (0.31)	15.8 (1.16)	52.5 (4.53)	77.5 (5.05)	37.4
DAP+Zn	5.39 (0.22)	17.4 (0.47)	86.3 (0.63)	109 (4.23)	54.4
DAP+Cu	3.81 (0.08)	16.7 (1.24)	53.6 (1.60)	60.7 (3.91)	33.7
Zn	3.47 (0.36)	23.4 (0.09)	79.5 (2.26)	84.9 (5.96)	47.8
Cu	2.89 (0.14)	12.1 (0.42)	35.7 (1.71)	53.7 (3.52)	26.1
LSD (0.05)	0.92	2.9	8.1	15.8	

ANOVA for the total uptake of Zn by wheat

Sources	df	Sum of squares	Mean square	F	P>F
Treatment (Trt)	8	10562	1320.3	47.96	0.0001
Time	3	102790	34263	1244	0.0001
Trt x Time	24	7314.8	304.8	11.07	0.0001
Error	72	1981.9	27.53		
Total	107	122649			

† Standard error of mean (n=3)

Appendix 11 ANOVA for the concentration of Cu, P and Zn in wheat grain

Sources	df	Sum of squares	Mean square	F	P>F
Concentration of Cu					
Treatment	8	36.58	4.573	35.58	0.0001
Error	18	2.452	0.136		
Total	26	39.03			
Concentration of P					
Treatment	8	19.53	2.44	12.19	0.0001
Error	18	3.605	0.20		
Total	26	23.14			
Concentration of Zn					
Treatment	8	4053	506.7	8.85	0.0001
Error	18	1031	57.28		
Total	26	5085			

Appendix 12 ANOVA for the uptake of Cu, P and Zn by wheat grain

Sources	df	Sum of squares	Mean square	F	P>F
Uptake of Cu					
Treatment	8	79.15	9.89	54.38	0.0001
Error	18	3.275	0.182		
Total	26	82.43			
Uptake of P					
Treatment	8	9.62	1.20	15.85	0.0001
Error	18	1.37	0.08		
Total	26	11.0			
Uptake of Zn					
Treatment	8	1334	166.8	3.66	0.0106
Error	18	819.9	45.55		
Total	26	2154			

Appendix 13 ANOVA for the concentration of available (extractable) P, Cu and Zn in soil

Sources	df	Sum of squares	Mean square	F	P>F
Extractable P					
Treatment (Trt)	8	12260	1532.5	166.6	0.0001
Time	3	2870.4	956.79	104.0	0.0001
Trt x Time	24	1564.9	65.21	7.09	0.0001
Error	72	662.31	9.198		
Total	107	17357			
Extractable Cu					
Treatment (Trt)	8	493.7	61.72	1972	0.0001
Time	3	3.158	1.053	33.65	0.0001
Trt x Time	24	19.08	0.795	25.40	0.0001
Error	72	2.253	0.031		
Total	107	518.2			
Extractable Zn					
Treatment (Trt)	8	2085	260.6	1712	0.0001
Time	3	66.79	22.27	146.3	0.0001
Trt x Time	24	66.55	2.773	18.21	0.001
Error	72	10.96	0.152		
Total	107	2229			

Appendix 14 ANOVA for the sorbed P and the Kd for sorption of P

Sources	df	Sum of squares	Mean square	F	P>F
Sorbed P					
Pretreatment	5	7846	1569	99999	0.000
Error	18	0.097	0.005		
Total	23	7846.5			
Kd for the sorption of P					
Pretreatment	5	156.1	31.23	949.8	0.0001
Error	18	0.592	0.033		
Total	23	156.71			

Appendix 15 ANOVA for the sorbed Cu and Kd for Cu sorption in the second equilibration, and Cu desorption in third equilibration

Sources	df	Sum of squares	Mean square	F	P>F
Cu sorption (second equilibration)					
†Concentration (C)	4	1131	282.8	99999	0.000
Pretreatment (T)	6	1.999	0.333	498.4	0.0001
C x T	24	0.971	0.040	60.52	0.0001
Error	35	0.023	0.0001		
Total	69	1134.1			
Kd of sorbed Cu (second equilibration)					
Concentration (C)	4	367.13	91.78	1.67	0.179
Pretreatment (T)	6	16221	2703	49.2	0.0001
C x T	24	3564	148.5	2.70	0.0037
Error	35	1925	55.01		
Total	69	22078			
Desorbed Cu (third equilibration)					
Concentration (C)	5	315.3	63.05	3399	0.001
Pretreatment (T)	6	48.40	8.07	434.8	0.0001
C x T	30	49.26	1.64	88.51	0.0001
Error	42	0.779	0.0186		
Total	83	413.7			

† Concentration of Cu

Appendix 16 The values of parameters (K and n) in the Freundlich equations for Cu sorption as influenced by the P pretreatments

Treatments	K	n	R^2
Control	12.9 (0.41)†	1.50 (0.13)	0.99
APP25	14.0 (0.34)	1.65 (0.10)	0.99
APP50	16.1 (0.41)	1.16 (0.06)	0.99
APP75	13.0 (0.26)	1.26 (0.07)	0.97
DAP25	19.9 (1.24)	1.78 (0.17)	0.99
DAP50	45.3 (5.19)	1.15 (0.07)	0.99
DAP75	132 (17.3)	0.57 (0.04)	0.99

† Standard error of estimate

Equations showing the relationship between the amount of sorbed Cu (X) and the amount of Cu that is subsequently desorbed (Y)

Treatments	Equations	R^2
Control	$Y = 0.12\ (0.03)^{\dagger} + 0.10X\ (0.00) + 0.040X^2\ (0.00)$	0.99
APP25	$Y = 0.16\ (0.02) + 0.10X\ (0.00) + 0.025X^2\ (0.01)$	0.99
APP50	$Y = 0.21\ (0.04) + 0.10X\ (0.00) + 0.018X^2\ (0.01)$	0.99
APP75	$Y = 0.25\ (0.02) + 0.10X\ (0.00) + 0.014X^2\ (0.01)$	0.99
DAP25	$Y = 0.17\ (0.04) + 0.10X\ (0.00) + 0.014X^2\ (0.01)$	0.99
DAP50	$Y = 0.15\ (0.01) + 0.10X\ (0.00) + 0.005X^2\ (0.00)$	0.99
DAP75	$Y = 0.20\ (0.01) + 0.10X\ (0.00) + 0.003X^2\ (0.01)$	0.99

† Standard error of estimate

Appendix 17 ANOVA for the desorbed P in the second and third equilibrations

Sources	df	Sum of squares	Mean square	F	P>F
Desorbed P (second equilibration)					
†Concentration (C)	5	70255.2	14051	59.61	0.0001
Pretreatment (T)	6	13117508	2186251	9275	0.0001
C x T	30	87848.3	2928.3	12.42	0.0001
Error	42	9899.7	235.71		
Total	83	13285511			
Desorbed P (third equilibration)					
Concentration (C)	5	2850.3	570.1	8.48	0.0001
Pretreatment (T)	6	2008177	334696	4979	0.0001
C x T	30	6625.8	220.9	3.29	0.0001
Error	42	2822.9	67.21		
Total	83	2020476			

† Concentration of Cu

Appendix 18 ANOVA for the sorption of Cu at 20, 40, 60 and 80 days after the pretreatment (sorption) with P

Sources	df	Sum of squares	Mean square	F	P>F
20 days					
†Concentration (C)	4	584.1	146.0	99999	0.000
Pretreatment (T)	4	0.019	0.005	73.51	0.0001
C x T	16	0.003	0.0002	2.66	0.0042
Error	50	0.003	0.00006		
Total	74	584.11			
40 days					
Concentration (C)	4	582.8	24.28	99999	0.000
Pretreatment (T)	4	0.020	0.0051	32.01	0.001
C x T	16	0.004	0.0002	1.36	0.199
Error	50	0.008	0.0002		
Total	74	582.79			
60 days					
Concentration (C)	4	581.3	145.3	99999	0.000
Pretreatment (T)	4	0.0208	0.005	10.02	0.0001
C x T	16	0.0104	0.0007	1.25	0.2633
Error	50	0.0260	0.0005		
Total	74	581.33			
80 days					
Concentration (C)	4	586.5	146.6	99999	0.000
Pretreatment (T)	4	0.002	0.0004	5.90	0.0006
C x T	16	0.001	0.00007	0.91	0.5582
Error	50	0.004	0.00008		
Total	74	586.496			

† Concentration of Cu

Appendix 19 ANOVA for the Kd of Cu sorption at 20, 40, 60 and 80 days after the P pretreatment

Sources	df	Sum of squares	Mean square	F	P>F
20 days					
†Concentration (C)	4	13480.4	3370.1	38.68	0.0001
Pretreatment (T)	4	8218.3	2054.6	23.58	0.0001
C x T	16	1832.3	114.52	1.31	0.2259
Error	50	4356.2	87.12		
Total	74	27887.2			
40 days					
Concentration (C)	4	6767.8	1691.9	27.85	0.0001
Pretreatment (T)	4	14305.7	3576.4	58.87	0.0001
C x T	16	677.12	42.32	0.70	0.7835
Error	50	3037.36	60.75		
Total	74	24788.0			
60 days					
Concentration (C)	4	6982.6	1745.7	34.95	0.0001
Pretreatment (T)	4	11078	2769.4	55.44	0.0001
C x T	16	245.81	15.36	0.31	0.9939
Error	50	2497.6	49.95		
Total	74	20803.6			
80 days					
Concentration (C)	4	29438	7360	42.48	0.0001
Pretreatment (T)	4	10053	2513	14.51	0.0001
C x T	16	4108.7	256.8	1.48	0.1443
Error	50	8662.7	173.3		
Total	74	52262.3			

† Concentration of Cu

Appendix 20 The values of parameters (K and n) in the Freundlich equation as influenced by the P pretreatments

	K	n	R^2
20 days			
Control	129 (25.0)†	0.65 (0.06)	0.97
APP15	69 (10.5)	0.85 (0.05)	0.98
APP30	77 (16.0)	0.83 (0.07)	0.97
DAP15	84 (24.0)	0.97 (0.14)	0.94
DAP30	57 (6.00)	1.11 (0.12)	0.97
40 days			
Control	56 (7.00)	0.89 (0.13)	0.96
APP15	43 (10.0)	1.02 (0.18)	0.95
APP30	53 (6.00)	0.95 (0.14)	0.96
DAP15	59 (7.00)	0.92 (0.14)	0.96
DAP30	73 (20.0)	0.97 (0.13)	0.97
60 days			
Control	31 (13.0)	1.18 (0.36)	0.83
APP15	42 (11.0)	0.95 (0.14)	0.96
APP30	50 (16.0)	0.87 (0.13)	0.96
DAP15	55 (17.0)	0.85 (0.13)	0.96
DAP30	125 (16.0)	0.72 (0.05)	0.96
80 days			
Control	70 (19.0)	1.00 (0.09)	0.98
APP15	64 (11.0)	1.03 (0.15)	0.96
APP30	58 (7.00)	1.09 (0.15)	0.96
DAP15	76 (23.0)	0.96 (0.13)	0.96
DAP30	99 (37.0)	0.92 (0.13)	0.96

† Standard error of estimate

Appendix 21 ANOVA for the desorption of P at 40, 60 and 80 days after P pretreatment

Sources	df	Sum of squares	Mean square	F	P>F
40 days					
Pretreatment (T)	4	7.507	1.877	39.62	0.0001
†Concentration (C)	5	0.8006	0.160	3.38	0.0093
C x T	20	0.9093	0.045	0.96	0.519
Error	60	2.842	0.047		
Total	89	12.06			
60 days					
Pretreatment (T)	4	5.258	1.314	490	0.0001
Concentration (C)	5	0.0198	0.0039	1.48	0.2097
C x T	20	0.0462	0.0023	0.86	0.6305
Error	60	0.1607	0.0027		
Total	89	5.485			
80 days					
Pretreatment (T)	4	3.803	0.9507	54.46	0.0001
Concentration (C)	5	0.371	0.0743	4.26	0.0022
C x T	20	0.387	0.0193	1.11	0.3647
Error	60	1.047	0.0175		
Total	89	5.609			

† Concentration of Cu

Appendix 22 Influence of APP and DAP pretreatment on the mean equilibrium concentration of Cu in solution at different reaction times and temperatures

	Time of reaction (h)								
Pretreatments	0.25	0.50	1.00	2.00	4.00	8.00	16.00	24.00	Mean
			µmol Cu L^{-1}						
281 K									
Control	4.30	3.29	3.06	3.03	2.61	2.86	3.08	3.05	3.16
APP	4.85	4.85	4.79	4.55	4.48	4.17	4.27	4.77	4.59
DAP	3.64	3.61	3.43	3.33	3.16	3.07	3.20	3.75	3.39
291 K									
Control	4.96	4.15	3.56	2.97	2.68	2.53	2.60	2.83	3.28
APP	5.21	5.15	4.94	4.80	4.12	4.63	4.22	4.75	4.73
DAP	4.01	3.84	3.54	3.09	3.10	3.49	3.45	4.04	3.57
301 K									
Control	5.38	4.39	3.75	3.42	2.76	2.56	2.60	2.50	3.42
APP	4.49	4.42	4.38	4.27	3.41	5.10	5.26	5.52	4.64
DAP	4.21	3.49	3.46	3.35	2.86	4.21	4.50	4.77	3.86

Appendix 23 Dependence of rate constant (k) on temperature (T) for Cu and P depletion

	Regression equation	R^2
Cu depletion		
Control	$\ln k = 4.54 - 1911.79\ (1/T)$	0.82
APP	$\ln k = 13.14 - 4709.32\ (1/T)$	0.86
DAP	$\ln k = 8.59 - 3322.99\ (1/T)$	0.91
P depletion		
APP	$\ln k = 1.15 - 1346.71\ (1/T)$	0.76
DAP	$\ln k = 3.10 - 1938.48\ (1/T)$	0.97

Appendix 24 Influence of P sources on the mean equilibrium concentration of P at different reaction times and temperatures

	Time of reaction (h)								
Treatments	0.25	0.50	1.00	2.00	4.00	8.00	16.00	24.00	Mean
	millimol P L^{-1}								
281 K									
APP	0.236	0.231	0.223	0.216	0.196	0.190	0.239	0.238	0.221
DAP	0.404	0.381	0.378	0.357	0.340	0.331	0.338	0.343	0.359
291 K									
APP	0.282	0.258	0.251	0.238	0.227	0.216	0.232	0.225	0.241
DAP	0.356	0.336	0.335	0.305	0.288	0.283	0.304	0.309	0.315
301 K									
APP	0.292	0.277	0.273	0.256	0.220	0.217	0.211	0.202	0.244
DAP	0.410	0.411	0.402	0.376	0.334	0.316	0.305	0.281	0.354